ON ANOMALOUS MONOLAYER ADSORPTION

by

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Prepared on June 24, 1954 for distribution according to the list for this project provided by the Office of Naval Research.

This paper constitutes a technical report of work done under Contract N7-onr-33005 of Project NR 010-603

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SUMMARY

An attempt has been made in this investigation to find out if the anomalous adsorption of helium at low temperatures, as observed first by Schaeffer, Smith and Wendell and later by Long and Meyer and also by Frederiske and Gorter, can be explained on the hypothesis that the surface of adsorption perturbs the electron wave functions of the adsorbed atoms so as to give rise to increased van der Waal attraction between them. We find an increase in attraction for hydrogen atoms but for helium atoms no appreciable increase in attraction is found out. The investigation leads us to believe that the excess adsorption in case of helium may be due to some other cause and the possibility of diffusion of the helium atoms into the solid through the adsorbing surface is pointed out.

On Anomalous Monolayer Adsorption

The early work on the adsorption of helium on solids was performed at quite low pressures (< 1 mm Hg), and consequently at saturations well below 1%. The preliminary work of Keesom and Schmidt[1] was followed by that of Keesom and Schweers[2]. The data showed that even at these low saturations a considerable adsorption occurs.

The adsorption of a rare gas such as helium should, at low saturations, be the case nearest to the conditions assumed in the derivation of the Langmuir[3] isotherm; however the data could not be fitted to the Langmuir equation. From later work, to be discussed below, it was found that the volume of helium adsorbed is quite anomalous; also, the data of Schweers show that the heat of adsorption decreases from almost 100 cal/mole at about 10% coverage to about 40 cal/mole when approaching completion of a monolayer. Since the Langmuir equation assumes no interaction between adsorbed particles (heat of adsorption independent of coverage) obviously the isotherm cannot be applied to the case of helium.

Later work was devoted to multilayer adsorption. Frederiske and Gorter[4] measured isotherms on Jeweller's rouge (Fe_2O_3) and on steel from 1.39°K to 2.26°K; Schaeffer, Smith and Wendell[5] measured isotherms on two different carbon adsorbents at the b.p. Long and Meyer[6] investigated adsorption on Fe_2O_3 at 1.53°K to 2.45°K; Mastrangelo and Aston[7] reported isotherms on TiO_2 at 2.41°K; and Strauss[8] has measured a series of eight isotherms on Fe_2O_3 at temperatures ranging from 1.59°K to 4.21°K.

Schaeffer, Smith and Wendell were the first to derive the volume adsorbed in the first layer. They determined the surface areas of their carbon adsorbents from adsorption isotherms of nitrogen, for which the adsorbed volume is well known. Using this as a comparison, they found that volume adsorbed for helium at the b.p. is far greater than that calculated from the surface area of the adsorbents and the cross-section of helium atom, as derived from the density of liquid helium. In almost all

other cases, these two values differ for spherical molecules by only a few percent.

The subsequent data of Frederiske and Gorter (1950) and Long and Meyer (1949) for adsorption on Fe_2O_3 confirmed these results. The density of adsorbed helium in the first monolayer is much higher than that of liquid at the same temperature. At temperatures below 2^oK, values up to four times the liquid density were observed; in the liquid helium the spacing of helium atoms is approximately 4Å.U., whereas in the first adsorbed layer it is reduced to values as low as 2.0Å.U. corresponding roughly to gas kinetic diameter of 2.1Å.U.

Long and Meyer (1949) also showed that such data cannot be fitted with the B.E.T.[9] theory of multilayer adsorption. The B.E.T. theory assumes that the site of an atom adsorbed in the first layer is a potential site for atoms in the higher layers. If, however, the first layer is of much higher density than the liquid, and therefore than that of higher layers (which must rapidly approach liquid density, provided the attractive forces are van der Waal in origin) then it contains more atoms per unit area than the next higher layer can accommodate. Band[10] showed, however, that even in this case it is justified to use the formalism of B.E.T. theory. He included a correction for the anomalous packing in the first layer and found the resulting isotherm agreeing fairly well with the observed isotherms for helium at low temperatures. It is pointed out in the above work that one can calculate the number filling the first layer from spacing in the liquid phase only if no anomalous packing occurs and also that the monolayer isotherm is altered not only by anomalous packing, but also by the fact that the energy of adsorption becomes a function of coverage even below one layer. The modified isotherms are deduced from a class of functions assumed for the dependence of monolayer adsorption energy on fractional coverage.

Several qualitative arguments have been advanced for the anomalous packing in the first layer. Long and Meyer have suggested that in the adsorbed film, interactions with the wall, much stronger than the van der Waal's forces of helium -

helium interaction, overcomes the repulsive action of the zero-point energy, which causes the liquid phase to be greatly blown-up, with the result that the first layer is compressed to about gas kinetic diameter i.e. the diameter of the electronic shell of the helium atom. As a consequence on filling up the first layer, the repulsive action of zero-point energy must counteract more and more the attractive forces of the wall, and thus the effective heat of adsorption should drop strongly as first layer becomes occupied. This argument is borne out by the data of Schweers previously mentioned. Evidently, in the case of helium, the zero-point energy provides an energy of interaction of the same order of magnitude as the heat of adsorption itself. On the completion of the first layer the forces of the wall are to a great extent balanced by the zero point energy, and the heat of adsorption is then only slightly higher than the heat of vaporization of bulk liquid.

The experiments as indicated above have shown that helium is compressed in the first layer to the gas kinetic diameter which is lower than the van der Waal minimum for helium - helium interaction. Margenau[11] has calculated the minimum distance for two helium atoms taking dipole - dipole, dipole - quadrupole and quadrupole - quadrupole interactions into account and obtains a value 2.8Å which is less than the value 2.96Å.U. obtained by Slater and Kirkwood[12]. The mutual interaction energy curve obtained by Margenau (loc.cit) shows that there is a huge amount of repulsion even if we try to bring the helium atoms to a distance of about 2.4Å.U. So that if the atoms are packed in the first layer with a spacing of about 2Å.U. then these repulsive forces have to be overcome by some forces due to adsorbing solid surface. An attempt has been made in this investigation to recalculate the helium - helium van der Waal interaction after the wave functions of the electrons of helium atoms have been perturbed by the interaction of the solid surface. The effect of the surface has been taken into account by postulating an electrical field F acting on the adsorbed atoms and under the effect of this field we find the perturbed eigenfunction of the

electrons of the atom in the ground state. Then using these perturbed wave functions we calculate the changed interaction energy between the adsorbed atoms arranged on the surface as polarized dipoles with their polarity in the opposite directions. First the case of adsorbed monatomic hydrogen is worked out because the problem is simpler and gives an insight into the method. Since the range of valence forces is much smaller than van der Waal forces we can safely treat the hydrogen atoms at a distance corresponding to van der Waal forces to be quite far removed from the formation of any molecules.

For a hydrogen atom the unperturbed ground state (n = 1) is $\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$ where a_0 is first Bohr radius of hydrogen atom and the next higher state (n = 2) has four eigenfunctions

$$\left.\begin{aligned}
\psi_{200} &= \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}} \\
\psi_{210} &= \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)\cos\theta\, e^{-\frac{r}{2a_0}} \\
\psi_{21\bar{1}} &= \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}\sin\theta\sin\phi \\
\psi_{211} &= \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}\sin\theta\cos\phi
\end{aligned}\right\} \qquad (1)$$

The state n = 2 is thus four fold degenerate. If we consider the adsorbing surface as (x,y) plane, then F acts in the z-direction and so the potential energy of the electron in this electric field is $L = -Fez = -Fer\cos\theta$. This perturbing field splits the four fold degenerate state n = 2 into two single states and one doubly degenerate state. If the effect of states n = 3 and higher is neglected one obtains, using the formalism of the perturbation theory for the degenerate case, the perturbed wave function for the ground state

$$\psi_{100}^{\prime(a)} = \psi_{100}^{(a)} - \frac{128}{243} Fea_0 \left\{ \frac{\frac{1}{\sqrt{2}}\left(\psi_{200}^{(a)} - \psi_{210}^{(a)}\right)}{\frac{3e^2}{8a_0} - 3Fea_0} \right\} + \frac{128}{243} Fea_0 \left\{ \frac{\frac{1}{\sqrt{2}}\left(\psi_{200}^{(a)} + \psi_{210}^{(a)}\right)}{\frac{3e^2}{8a_0} + 3Fea_0} \right\} \quad (2)$$

We call an atom whose perturbed wave function is given by (2) as atom "a". Another atom which is adsorbed with opposite polarity we call atom "b" and this perturbed wave function for the ground state

$$\psi_{100}^{\prime(b)} = \psi_{100}^{(b)} + \frac{128}{243} Fea_0 \left\{ \frac{\frac{1}{\sqrt{2}}\left(\psi_{200}^{(b)} + \psi_{210}^{(b)}\right)}{\frac{3e^2}{8a_0} - 3Fea_0} \right\} - \frac{128}{243} Fea_0 \left\{ \frac{\frac{1}{\sqrt{2}}\left(\psi_{200}^{(b)} - \psi_{210}^{(b)}\right)}{\frac{3e^2}{8a_0} + 3Fea_0} \right\} \quad (3)$$

where we have changed the sign of F and also it is understood that the wave function $\frac{1}{\sqrt{2}}\left(\psi_{200}^{(b)} - \psi_{210}^{(b)}\right)$ corresponds now to energy $E_2^0 + 3Fea_0$ and $\frac{1}{\sqrt{2}}\left(\psi_{200}^{(b)} + \psi_{210}^{(b)}\right)$ to the energy state $E_2^0 - 3Fea_0$ while it was the reverse for the atom "a".

The energy of interaction between two hydrogen atoms is composed of several multipole terms[13] with monopole term being zero. We take the first appreciable term only which is called the dipole term given by

$$H' = \frac{e^2}{R^3}\left(x_1 x_2 + y_1 y_2 - 2 z_1 z_2\right) \quad (4)$$

where e is the electronic charge, R the internuclear distance of the two atoms while (x_1, y_1, z_1) and (x_2, y_2, z_2) are the coordinates of two electrons, or if we use spherical polar coordinates (r, θ, ϕ) with z-axis on the surface and along the line joining two atomic nuclei, we have

$$H' = \frac{e^2}{R^3}\Big[r_{1k} r_{2l} \sin\theta_1 \sin\theta_2 \cos\phi_1 \cos\phi_2 + r_{1k} r_{2l} \sin\theta_1 \sin\theta_2 \sin\phi_1 \sin\phi_2 - 2 r_{1k} r_{2l} \cos\theta_1 \cos\theta_2 \Big] \quad (5)$$

In the evaluation of mutual interaction energy the first order term $\int \psi_1^{2(a)} H' \psi_1^{2(b)} d\tau_1 d\tau_2 \Big/ \int \psi_1^{2(a)} \psi_2^{2(b)} d\tau_1 d\tau_2$ is zero and hence the main contribution comes from the second order term

$$W_R = -\frac{(H'^2)_{oo}}{2(E_2^\circ - E_1^\circ)} \tag{6}$$

where

$$(H'^2)_{oo} = \frac{\int \psi_1^{2(a)} H'^2 \psi_1^{2(b)} d\tau_1 d\tau_2}{\int \psi_1^{2(a)} \psi_1^{2(b)} d\tau_1 d\tau_2} \tag{7}$$

We shall keep in mind that in the evaluation of above integrals we shall change cos θ occurring in ψ_{1s_0} to $\alpha\text{-}\beta$ in order to take account of the change in z-axis direction. The numerator of (7) reduces to

$$\frac{3e^4}{R^6}\left[\int r_{1a}^2 \psi_{100}^{2(a)} \sin^2\theta_1 \cos^2\phi_1 \, d\tau_1 \int r_{2b}^2 \psi_{100}^{2(b)} \sin^2\theta_2 \cos^2\phi_2 \, d\tau_2 \right.$$
$$\left. + \frac{4e^4}{R^6}\int \psi_{100}^{2(a)} r_{1a}^2 \cos^2\theta_1 \, d\tau_1 \int \psi_{100}^{2(b)} r_{2b}^2 \cos^2\theta_2 \, d\tau_2 \right. \tag{8}$$

and these on evaluation yield

$$\frac{3e^4}{R^6}\left[\left\{a_0^2 + \left(\frac{.3725\,Fea_0}{\frac{3e^2}{8a_0} - 3Fea_0}\right)^2 \times 73.33a_0^2 + \left(\frac{.3725\,Fea_0}{\frac{3e^2}{8a_0} + 3Fea_0}\right)^2 \times 2.67\,a_0^2\right.\right.$$
$$+ \left(\frac{.7450\,Fea_0}{\frac{3e^2}{8a_0} - 3Fea_0}\right) \times 4.282a_0^2 + \left(\frac{.7450\,Fea_0}{\frac{3e^2}{8a_0} + 3Fea_0}\right) \times 2.396a_0^2$$
$$\left. + \left(\frac{(.5267\,Fea_0)^2}{\left(\frac{3e^2}{8a_0}\right)^2 - (3Fea_0)^2}\right) \times 18a_0^2\right\} \times \left\{a_0^2 + \left(\frac{.3725\,Fea_0}{\frac{3e^2}{8a_0} - 3Fea_0}\right)^2 \times 2.67a_0^2\right.$$
$$+ \left(\frac{.3725\,Fea_0}{\frac{3e^2}{8a_0} + 3Fea_0}\right)^2 \times 73.33a_0^2 + \left(\frac{.7450\,Fea_0}{\frac{3e^2}{8a_0} - 3Fea_0}\right) \times 2.396a_0^2$$

$$+\left(\frac{.7450\,Fea_0}{\frac{3e^2}{8a_0}+3Fea_0}\right)\times 4.282\,a_0^2+\left(\frac{(.5267\,Fea_0)^2}{\left(\frac{3e^2}{8a_0}\right)^2-(3Fea_0)^2}\right)\times 10\,a_0^2\Bigg\}\Bigg]+\frac{4e^4}{R^6}\Bigg[\Bigg[\Bigg\{a_0^2+$$

$$\left(\frac{.3725\,Fea_0}{\frac{3e^2}{8a_0}-3Fea_0}\right)^2\times 49.55\,a_0^2+\left(\frac{.3725\,Fea_0}{\frac{3e^2}{8a_0}+3Fea_0}\right)^2\times 2.45\,a_0^2+\left(\frac{.7450\,Fea_0}{\frac{3e^2}{8a_0}-3Fea_0}\right)\times 2.45\,a_0^2$$

$$+\left(\frac{.7450\,Fea_0}{\frac{3e^2}{8a_0}+3Fea_0}\right)\times .468\,a_0^2-\left(\frac{(.5267\,Fea_0)^2}{\left(\frac{3e^2}{8a_0}\right)^2-(3Fea_0)^2}\right)\times 2a_0^2\Bigg\}\times\Bigg\{a_0^2+\left(\frac{.3725\,Fea_0}{\frac{3e^2}{8a_0}-3Fea_0}\right)^2$$

$$\times 2.45\,a_0^2+\left(\frac{.3795\,Fea_0}{\frac{3e^2}{8a_0}+3Fea_0}\right)^2\times 49.55\,a_0^2+\left(\frac{.7450\,Fea_0}{\frac{3e^2}{8a_0}-3Fea_0}\right)\times .468\,a_0^2$$

$$+\left(\frac{.7450\,Fea_0}{\frac{3e^2}{8a_0}+3Fea_0}\right)\times 2.45\,a_0^2-\left(\frac{(.5267\,Fea_0)^2}{\left(\frac{3e^2}{8a_0}\right)^2-(3Fea_0)^2}\right)\times 2a_0^2\Bigg\}\Bigg]\Bigg] \tag{9}$$

In order to find a numerical estimate of the above expression we need the value of F which we derive from the data of adsorption of hydrogen on glass as found out by Keesom and Schweers (loc. cit). They found that adsorption energy for hydrogen on glass is about 1000 cal/mole which we equate to $1/2\times 2\alpha N F^2$ where N is the Avogadro number and α is the polarizability of the hydrogen atom which has a value $\frac{9}{2}a_0^3$.

This gives

$$F^2=\frac{2\times 500\times 4.18\times 10^7}{\frac{9}{2}a_0^3\times N}=\frac{4.18\times 10^{10}}{.677\times 10^{-24}\times 6\times 10^{23}}$$

$$=10.29\times 10^{10}\,(e.s.u)^2$$

or

$$F=3.21\times 10^5\ e.s.u \tag{10}$$

and using this value of F in (9) we get the numerator of (7) as

$$\frac{2e^4}{R^6}\left(a_0^2 + \cdot 3035 a_0^2\right)\left(a_0^2 + \cdot 2654 a_0^2\right) + \frac{4e^4}{R^6}\left(a_0^2 + \cdot 1448 a_0^2\right)\left(a_0^2 + \cdot 1220 a_0^2\right)$$

$$= \frac{6e^4 a_0^4}{R^6}\left(1 \cdot 4060\right)$$

$$= \frac{6e^4 a_0^4}{R^6}\left(1 + \cdot 4060\right) \tag{11}$$

From equations (2) and (3) we also notice that the denominator of (7) is almost equal to one as the first order terms in F integrate out to zero and F^2 part is very small. Thus we obtain

$$W_R = -\frac{6e^4 a_0^4}{R^6} \times \frac{(1 + \cdot 4060)}{3e^2/4a_0}$$

$$= -\frac{8e^4 a_0^5}{R^6}\left(1 + \cdot 4060\right) \tag{12}$$

Showing an increase in the attraction between absorbed atoms of some 40%.

We now return to our main problem of finding, if the helium atoms, adsorbed on the plane surface according to this model, will have enough increased mutual interaction so as to explain the closer packing as evidenced by experimental results. Since the wave function of a helium atom in the ground st te is not known in the closed form we shall use the most promising one obtained by variational method and used by Hasse[14] to find out the most accurate value of the polarizability of the helium atom in an electrical field. The unperturbed wave function for the ground state is

$$\Psi_1^0 = e^{-n(r_1 + r_2)}\left(1 + c\, r_{12}\right) \tag{13}$$

where r_1 and r_2 are the distances of two electrons from the center of the nucleus and r_{12} is the interelectronic distance. The distances r_1, r_2 and r_{12} are expressed in dimensionless Hartree units where the unit of distance is the first Bohr radius ($a_0 = .528 \times 10^{-8}$ cm.); N and C are constants having the values

$$C = .364$$

$$N = 1.849$$

The perturbed wave-function is

$$\Psi_1 = e^{-n(r_1+r_2)}(1+c\,r_{12})(1 + A_1 x_1 + A_2 x_2 + B_1 r_1 x_1 + B_2 r_2 x_2) \qquad (14)$$

where x_1 and x_2 are the x-coordinates of the two electrons expressed in Hartree units and A_1, B_1, A_2, B_2 are dimensionless constants having the values

$$A_1 = A_2 = 0.3844 \; F$$

$$B_1 = B_2 = 0.3845 \; F$$

F here is dimensionless force expressed in Hartree units. The coordinates of the electrons of adsorbed atoms referred to a rectangular system of axes with adsorbing surface as y-z plane, the line joining the nuclei of two atoms as z-axis and with x-axis perpendicular to the surface.

Since A_1, B_1, A_2, B_2 are nearly equal, we write the perturbed wave function as

$$\Psi_1 = e^{-n(r_1+r_2)}(1+c\,r_{12})\left[1 + A(x_1 + x_2 + r_1 x_1 + r_2 x_2)\right] \qquad (15)$$

where we put A = 0.3845 F. For another helium atom adsorbed on the surface with the electrical force acting in the opposite direction, the wave function would be

$$\Psi_2 = e^{-n(r_3+r_4)}(1+c\,r_{34})\left[1 - A(x_3 + x_4 + r_3 x_3 + r_4 x_4)\right] \qquad (16)$$

where we have called the electrons associated with atom 2 as electrons 3 and 4. Using these we shall calculate the interaction energy between two adsorbed atoms keeping in mind that we have neglected any overlap forces due to quantum mechanical exchange. The first term in the classical coulomb potential energy between two neutral helium atoms with their nuclear distance R apart and with electron coordinates as (x_1, y_1, z_1), (x_2, y_2, z_2), (x_3, y_3, z_3) and (x_4, y_4, z_4) is

$$V = \frac{e^2}{R^3}\Big[(x_1x_3 + y_1y_3 - 2z_1z_3) + (x_1x_4 + y_1y_4 - 2z_1z_4) + (x_2x_3 + y_2y_3 - 2z_2z_3) + (x_2x_4 + y_2y_4 - 2z_2z_4)\Big] \tag{17}$$

This, when expressed in Hartree units (e^2/a_0), is given by

$$V = \frac{1}{R^3}\Big[(x_1x_3 + y_1y_3 - 2z_1z_3) + (x_1x_4 + y_1y_4 - 2z_1z_4) + (x_2x_3 + y_2y_3 - 2z_2z_3) + (x_2x_4 + y_2y_4 - 2z_2z_4)\Big] \tag{18}$$

and the interaction energies of the first and second order are

$$\Delta E_1 = \frac{\iiiint \psi_1^2 V \psi_2^2 \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4}{\iiiint \psi_1^2 \psi_2^2 \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4} \tag{19}$$

$$\Delta E_2 = -\frac{\iiiint \psi_1^2 V^2 \psi_2^2 \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4 \Big/ \iiiint \psi_1^2 \psi_2^2 \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4}{E_{11} + E_{21} - E_{12} - E_{22}} \tag{20}$$

We shall now evaluate the integrals appearing in the above expressions for the interaction energy. Each integral breaks up into several elementary integrals whose values are given in the Appendixes at the end. Using those we get the interaction energy in Hartree units.

$$\Delta E_1 + \Delta E_2 = -\frac{.4128\,F^2}{R^3(.2671 + .3606\,F^2 + .1216\,F^4)} - \frac{(.8256 + 2.8110\,F^2 + 2.2181\,F^4)}{R^6(.2671 + .3606\,F^2 + .1216\,F^4)} \Big/ E_{11} + E_{21} - E_{12} - E_{22} \tag{21}$$

where $E_{11} + E_{21}$ is the total energy of the two electrons of an atom in Hartree units when both electrons are in the ground state, and $E_{12} + E_{22}$ is the total energy of the two electrons when both are in the first excited state. These values[15], after correction for the Coulomb repulsion, are in Hartree units numerically equal to

$$E_{11} + E_{21} = 2.75$$

and

$$E_{12} + E_{22} = .70$$

giving

$$E_{11} + E_{21} - E_{12} - E_{22} = 2.05$$

Thus

$$\Delta E_1 + \Delta E_2 = -\frac{.4128\,F^2}{R^3(.2671 + .3606\,F^2 + .1216\,F^4)} - \frac{(.8256 + 2.8110\,F^2 + 2.2181\,F^4)}{R^6(.2671 + .3606\,F^2 + .1216\,F^4) \times 2.05} \tag{22}$$

where first term is a dipole - dipole interaction energy and second is van der Waal term. If there is no field i.e. atoms are free, we have $F = 0$ and in this case interaction energy is

$$-\frac{.8256}{.2671 \times 2.05} \quad \text{Hartree units} \tag{23}$$

$$= -\frac{65.8 \times 10^{-12}}{(R/a_0)^6}$$

where we have replaced R by R/a_0, R being in cms.

This value agrees fairly well with Slater's value $-\dfrac{68\times10^{-12}}{(R/a_0)^6}$ ergs.

To evaluate the complete value of interaction energy we need an estimate of the value of F from the energy of adsorption for helium gas. This has been measured experimentally and has a maximum value of about 100 cal/mole at zero coverage. If we use this we have field intensity in ordinary units given by $\frac{1}{2}\alpha E^2 N$ where

$$\frac{1}{2}\alpha E^2 N = 100 \times 4.18 \times 10^7$$

or

$$E^2 = \frac{2 \times 100 \times 4.18 \times 10^7}{.206 \times 10^{-24} \times 6.03 \times 10^{23}} = 7.41 \times 10^{10} \frac{\text{dynes}^2}{(\text{e.s.u charge})}$$

or

$$E = 2.722 \times 10^5 \frac{\text{dynes}}{\text{e.s.u. charge}}$$

Expressed in Hartree units this is

$$F = E \times \frac{a_0^2}{e}$$

$$= \frac{2.722 \times 10^5 \times (.5281)^2 \times 10^{-16}}{4.80 \times 10^{-10}} \tag{24}$$

$$= .0158$$

and therefore

$$\Delta E_1 + \Delta E_2 = -\left[\frac{.000105}{R^3 \times .2671} + \frac{.8265}{R^6 \times 2.05 \times .2671}\right] = -\left[\frac{.000393}{R^3} + \frac{1.509}{R^6}\right]$$

$$= -\left[\frac{.0172}{(R/a_0)^3} + \frac{65.85}{(R/a_0)^6}\right] \times 10^{-12} \text{ ergs} \tag{25}$$

Next we have evaluated the first order interaction ΔE_1 in Appendix D using symmetrized wave functions. In this case ΔE_1 is obtained to be

$$\Delta E_1 = \frac{.0039}{(R/a_0)^3} \times 10^{-12} \quad \text{ergs.}$$

which is a repulsive term because of overlap integrals which enter such a calculation. This value merely shows that dipole - dipole interaction is repulsive and so attraction will still be due to van der Waal force. The numerical value of ΔE_1 is very unrealistic because of the neglect of large number of terms in the expansion for $\mathcal{V}$.

The whole analysis definitely leads us to the conclusion that in the case of adsorption of helium on solid surfaces, the close packing cannot be due to the influence of the surface of adsorption in the sense that it increases the mutual attraction between the neighboring adsorbed atoms. Even if we extend this analysis to larger number of neighbors, the situation would not be essentially altered because the value obtained for interaction energy will have to be divided by the number of neighbors to give the mutual interaction energy between the atom under consideration and one of its neighbors.

In conclusion we are lead to believe that if the anomalous adsorption is a genuine phenomenon, the extra number of helium atoms probably diffuse through the adsorbing surface into the solid and do not remain confined to the surface.

APPENDIX A

The integral $\int \psi_1^2 \, \psi_2^2 \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4$ is equal to

$$\iint e^{-2n(r_1+r_2)} \left(1+2c\, r_{12} + c^2 r_{12}^2\right) \cdot \left[1 + 2A\left(x_1 + x_2 + r_1 x_1 + r_2 x_2\right) + A^2\left(x_1 + x_2 + r_1 x_1 + r_2 x_2\right)^2\right] d\tau_1 \, d\tau_2$$

$$\times \iint e^{-2n(r_3+r_4)} \left(1+2c\, r_{34} + c^2 r_{34}^2\right) \cdot \left[1 - 2A\left(x_3 + x_4 + r_3 x_3 + r_4 x_4\right) + A^2\left(x_3 + x_4 + r_3 x_3 + r_4 x_4\right)^2\right] d\tau_3 \, d\tau_4$$

$$= \iint e^{-2n(r_1+r_2)} \left(1+2c\, r_{12} + c^2 r_{12}^2\right) \cdot \Big[1 + 2A\left(x_1 + x_2 + r_1 x_1 + r_2 x_2\right) + A^2\big(x_1^2 + x_2^2$$
$$+ r_1^2 x_1^2 + r_2^2 x_2^2 + 2x_1 x_2 + 2r_1 x_1^2 + 2r_2 x_2^2 + 2r_1 x_1 x_2$$
$$+ 2r_2 x_1 x_2 + 2r_1 r_2 x_1 x_2\Big] d\tau_1 \, d\tau_2 \times \iint e^{-2n(r_3+r_4)} \left(1+2c\, r_{34} + c^2 r_{34}^2\right) \times$$
$$\Big[1 - 2A\left(x_3 + x_4 + r_3 x_3 + r_4 x_4\right) + A^2\big(x_3^2 + x_4^2 + r_3^2 x_3^2 + r_4^2 x_4^2$$
$$+ 2x_3 x_4 + 2r_3 x_3^2 + 2r_4 x_4^2 + 2r_3 x_3 x_4 + 2r_4 x_3 x_4$$
$$+ 2r_3 r_4 x_3 x_4\big)\Big] d\tau_3 \, d\tau_4 .$$

Each one of the above integrals breaks up into forty five integrals. The values of the integrals in the first set are the same as in the second set except for the fact that where +A occurs in the first set we have -A in the second. The integrals and their values are given below.

(1) $\displaystyle\iint e^{-2n(\tau_1+\tau_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2}{n^6} = .2469$

(2) $\displaystyle 2A\iint x_1\, e^{-2n(\tau_1+\tau_2)}\,d\tau_1\,d\tau_2 = 0$

(3) $\displaystyle 2A\iint \tau_1 x_1\, e^{-2n(\tau_1+\tau_2)}\,d\tau_1\,d\tau_2 = 0$

(4) $\displaystyle 2A\iint x_2\, e^{-2n(\tau_1+\tau_2)}\,d\tau_1\,d\tau_2 = 0$

(5) $\displaystyle 2A\iint \tau_2 x_2\, e^{-2n(\tau_1+\tau_2)}\,d\tau_1\,d\tau_2 = 0$

(6) $\displaystyle A^2\iint x_1^2\, e^{-2n(\tau_1+\tau_2)}\,d\tau_1\,d\tau_2 = \frac{A^2\pi^2}{n^8} = .0107\,F^2$

(7) $\displaystyle A^2\iint x_2^2\, e^{-2n(\tau_1+\tau_2)}\,d\tau_1\,d\tau_2 = \frac{A^2\pi^2}{n^8} = .0107\,F^2$

(8) $\displaystyle A^2\iint \tau_1^2 x_1^2\, e^{-2n(\tau_1+\tau_2)}\,d\tau_1\,d\tau_2 = \frac{15A^2\pi^2}{2n^{10}} = .0234\,F^2$

(9) $\displaystyle A^2\iint \tau_2^2 x_2^2\, e^{-2n(\tau_1+\tau_2)}\,d\tau_1\,d\tau_2 = \frac{15A^2\pi^2}{2n^{10}} = .0234\,F^2$

(10) $\displaystyle 2A^2\iint x_1 x_2\, e^{-2n(\tau_1+\tau_2)}\,d\tau_1\,d\tau_2 = 0$

(11) $\displaystyle 2A^2\iint \tau_1 x_1^2\, e^{-2n(\tau_1+\tau_2)}\,d\tau_1\,d\tau_2 = \frac{5A^2\pi^2}{n^9} = .0289\,F^2$

(12) $\displaystyle 2A^2\iint x_1 x_2 \tau_2\, e^{-2n(\tau_1+\tau_2)}\,d\tau_1\,d\tau_2 = 0$

$$(13) \quad 2A^2 \iint x_1 x_2 r_1 e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = 0$$

$$(14) \quad 2A^2 \iint r_2 x_2^2 e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = \frac{5A^2\pi^2}{n^9} = .0287 F^2$$

$$(15) \quad 2A^2 \iint r_1 r_2 x_1 x_2 e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = 0$$

$$(16) \quad 2c \iint r_{12} e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = \frac{35\pi^2 c}{5n^7} = .2126$$

$$(17) \quad 4Ac \iint r_{12} x_1 e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = 0$$

$$(18) \quad 4Ac \iint r_{12} x_2 e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = 0$$

$$(19) \quad 4Ac \iint r_{12} r_1 x_1 e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_3 = 0$$

$$(20) \quad 4Ac \iint r_{12} r_2 x_2 e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = 0$$

$$(21) \quad 2A^2c \iint r_{12} x_1^2 e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = \frac{\pi^2 A^2 c}{n^9} \times \frac{189}{32} = .01241 F^2$$

$$(22) \quad 2A^2c \iint r_{12} x_2^2 e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = \frac{\pi^2 A^2 c}{n^9} \times \frac{189}{32} = .01241 F^2$$

$$(23) \quad 2A^2c \iint r_{12} r_1^2 x_1^2 e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = \frac{5\pi^2 A^2 c}{n^{11}} \times \frac{2137}{256} = .0257 F^2$$

$$(24) \quad 2A^2c \iint r_{12} r_2^2 x_2^2 e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = \frac{5\pi^2 A^2 c}{n^{11}} \times \frac{2137}{256} = .0257 F^2$$

$$(25) \quad 4A^2c \iint r_{12} x_1 x_2 e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = 0$$

(26) $$4A^2c \iint r_{12}\, r_1\, x_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c}{n^{10}} \times \frac{2163}{64} = .0384\, F^2$$

(27) $$4A^2c \iint r_{12}\, x_1\, x_2\, r_2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = 0$$

(28) $$4A^2c \iint r_{12}\, x_1\, x_2\, r_1\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = 0$$

(29) $$4A^2c \iint r_{12}\, r_2\, x_2^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c}{n^{10}} \times \frac{2163}{64} = .0384\, F^2$$

(30) $$4A^2c \iint r_{12}\, x_1\, x_2\, r_1\, r_2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = 0$$

(31) $$c^2 \iint r_{12}^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{6\pi^2 c^2}{n^8} = .05743$$

(32) $$2Ac^2 \iint r_{12}^2\, x_2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = 0$$

(33) $$2Ac^2 \iint r_{12}^2\, x_1\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = 0$$

(34) $$2Ac^2 \iint r_{12}^2\, r_1\, x_1\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = 0$$

(35) $$2Ac^2 \iint r_{12}^2\, r_2\, x_2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = 0$$

(36) $$A^2c^2 \iint r_{12}^2\, x_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{n^{10}} \times \frac{21}{2} = .00435\, F^2$$

(37) $$A^2c^2 \iint r_{12}^2\, x_2^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{n^{10}} \times \frac{21}{2} = .00435\, F^2$$

(38) $$A^2c^2 \iint r_{12}^2\, r_1^2\, x_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{n^{12}} \times \frac{255}{2} = .01544\, F^2$$

(39) $$A^2c^2 \iint r_{12}^2\, r_2^2\, x_2^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{n^{12}} \times \frac{255}{2} = .01544\, F^2$$

$$(40) \quad 2A^2c^2 \iint r_{12}^2 \, x_1 x_2 \, e^{-2n(r_1+r_2)} \, dr_1 \, dr_2 = 0$$

$$(41) \quad 2A^2c^2 \iint r_{12}^2 \, r_1 \, x_1^2 \, e^{-2n(r_1+r_2)} \, dr_1 \, dr_2 = \frac{\pi^2 A^2 c^2}{n^{11}} \times \frac{135}{2} = .0151 \, F^2$$

$$(42) \quad 2A^2c^2 \iint r_{12}^2 \, x_1 x_2 r_2 \, e^{-2n(r_1+r_2)} \, dr_1 \, dr_2 = 0$$

$$(43) \quad 2A^2c^2 \iint r_{12}^2 \, x_1 x_2 r_1 \, e^{-2n(r_1+r_2)} \, dr_1 \, dr_2 = 0$$

$$(44) \quad 2A^2c^2 \iint r_{12}^2 \, r_2 \, x_2^2 \, e^{-2n(r_1+r_2)} \, dr_1 \, dr_2 = \frac{\pi^2 A^2 c^2}{n^{11}} \times \frac{135}{2} = .0151 \, F^2$$

$$(45) \quad 2A^2c^2 \iint r_{12}^2 \, r_1 r_2 \, x_1 x_2 \, e^{-2n(r_1+r_2)} \, dr_1 \, dr_2 = 0$$

The above integrals show that all the terms where A occurs are zero and so the two integrals

$$\iint \left[e^{-2n(r_1+r_2)} (1+cr_{12})^2 \left[1 + A(x_1+x_2+r_1x_1+r_2x_2) \right] \right]^2 dr_1 \, dr_2$$

and

$$\iint \left[e^{-2n(r_3+r_4)} (1+cr_{34})^2 \left[1 - A(x_3+x_4+r_3x_3+r_4x_4) \right] \right]^2 dr_3 \, dr_4$$

have the same value. Thus we have

$$\iiiint \psi_1^2 \psi_2^2 \, dr_1 \, dr_2 \, dr_3 \, dr_4 = \left(.5169 + .3488 \, F^2 \right)^2$$

$$= \left(.2671 + .3606 \, F^2 + .1216 \, F^4 \right)$$

APPENDIX B

The second integral $\iiiint \psi_1^* V \psi_2^2 \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4$

is

$$\frac{1}{R^3}\iiiint e^{-2n(r_1+r_2)}\left(1+2cr_{12}+c^2r_{12}^2\right)\Big[1+2A(x_1+x_2+r_1x_1+r_2x_2)+A^2(x_1^2+x_2^2+$$
$$r_1^2x_1^2+r_2^2x_2^2+2x_1x_2+2r_1x_1^2+2r_2x_2^2+2r_1x_1x_2$$
$$+2r_2x_1x_2+2x_1x_2r_1r_2\Big]\cdot\Big\{(x_1x_3+y_1y_3-2z_1z_3)+(x_1x_4+y_1y_4-2z_1z_4)$$
$$+(x_2x_3+y_2y_3-2z_2z_3)+(x_2x_4+y_2y_4-2z_2z_4)\Big\}\cdot e^{-2n(r_3+r_4)}$$
$$\left(1+2cr_{34}+c^2r_{34}^2\right)\Big[1-2A(x_3+x_4+r_3x_3+r_4x_4)+A^2(x_3^2+x_4^2+$$
$$r_3^2x_3^2+r_4^2x_4^2+2x_3x_4+2x_3^2r_3+2x_4^2r_4+2r_3x_3x_4$$
$$+2r_4x_3x_4+2r_3r_4x_3x_4)\Big]\,d\tau_1\,d\tau_2\,d\tau_3\,d\tau_4$$

$$=\frac{1}{R^3}\Big\{\iint e^{-2n(r_1+r_2)}\left(1+2cr_{12}+c^2r_{12}^2\right)\Big[1+2A(x_1+x_2+r_1x_1+r_2x_2)$$
$$+A^2(x_1^2+x_2^2+r_1^2x_1^2+r_2^2x_2^2+2x_1x_2+2r_1x_1^2+2r_2x_2^2$$
$$+2r_1x_1x_2+2r_2x_1x_2+2r_1r_2x_1x_2\Big]\,x_1\,d\tau_1\,d\tau_2\,\times$$
$$\iint e^{-2n(r_3+r_4)}\left(1+2cr_{34}+c^2r_{34}^2\right)\Big[1-2A(x_3+x_4+r_3x_3+r_4x_4)+A^2(x_3^2+$$
$$x_4^2+r_3^2x_3^2+r_4^2x_4^2+2x_3x_4+2r_3x_3^2+2r_4x_4^2+2r_3x_3x_4$$
$$+2r_4x_3x_4+2r_3r_4x_3x_4\Big]\,x_3\,d\tau_3\,d\tau_4$$
$$+\iint e^{-2n(r_1+r_2)}\left(1+2cr_{12}+c^2r_{12}^2\right)\Big[1+2A(x_1+x_2+r_1x_1+r_2x_2)+A^2(x_1^2+x_2^2$$
$$+r_1^2x_1^2+r_2^2x_2^2+2x_1x_2+2r_1x_1^2+2r_2x_2^2+2r_1x_1x_2+2r_2x_1x_2$$

$$+2\gamma_1\gamma_2 x_1 x_2\Big] z_1\, d\tau_1\, d\tau_2 \times \iint e^{-2n(\gamma_3+\gamma_4)} (1+2c\gamma_{34}+c^2\gamma_{34}^2)\Big[1-2A(x_3+$$

$$x_4+\gamma_3 x_3+\gamma_4 x_4) + A^2\big(x_3^2+x_4^2+\gamma_3^2 x_3^2+\gamma_4^2 x_4^2+2x_3x_4$$

$$+2\gamma_3 x_3^2+2\gamma_4 x_4^2+2\gamma_3 x_3 x_4+2\gamma_4 x_3 x_4$$

$$+2\gamma_3\gamma_4 x_3 x_4\big)\Big] z_3\, d\tau_3\, d\tau_4$$

$$-2\iint e^{-2n(\gamma_1+\gamma_2)}(1+2c\gamma_{12}+c^2\gamma_{12}^2)\Big[1+2A(x_1+x_2+\gamma_1 x_1+\gamma_2 x_2)$$

$$+A^2(x_1^2+x_2^2+\gamma_1^2 x_1^2+\gamma_2^2 x_2^2+2x_1x_2+2\gamma_1 x_1^2$$

$$+2\gamma_2 x_2^2+2\gamma_1 x_1 x_2+2\gamma_2 x_1 x_2+2\gamma_1\gamma_2 x_1 x_2\Big] z_1\, d\tau_1\, d\tau_2$$

$$\times\iint e^{-2n(\gamma_3+\gamma_4)}(1+2c\gamma_{34}+c^2\gamma_{34}^2)\Big[1-2A(x_3+x_4+\gamma_3 x_3+\gamma_4 x_4)+A^2(x_3^2+$$

$$x_4^2+\gamma_3^2 x_3^2+\gamma_4^2 x_4^2+2x_3x_4+2\gamma_3 x_3^2+2\gamma_4 x_4^2$$

$$+2\gamma_3 x_3 x_4+2\gamma_4 x_3 x_4+2\gamma_3\gamma_4 x_3 x_4\Big] z_3\, d\tau_3\, d\tau_4\Bigg\}$$

$+$ 3 more terms of the same type.

It can be seen clearly that in the above integrals the non-zero parts belong to the first one.

Thus

$$\iiiint \psi_1^2 V \psi_2^2\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4$$

$$=\frac{4}{R^3}\Bigg\{\iint e^{-2n(\gamma_1+\gamma_2)}(1+2c\gamma_{12}+c^2\gamma_{12}^2)\Big[1+2A(x_1+x_2+\gamma_1 x_1+\gamma_2 x_2)+A^2(x_1^2+x_2^2$$

$$+\gamma_1^2 x_1^2+\gamma_2^2 x_2^2+2x_1x_2+2\gamma_1 x_1^2+2\gamma_2 x_2^2+2\gamma_1 x_1 x_2$$

$$+2\gamma_2 x_1 x_2+2\gamma_1\gamma_2 x_1 x_2\Big] x_1\, d\tau_1\, d\tau_2$$

$$\times \iint e^{-2n(r_3+r_4)} (1+2c\,r_{34}+c^2 r_{34}^2)\Big[1-2A(x_3+x_4+r_3x_3+r_4x_4)+A^2(x_3^2+x_4^2$$
$$+r_3^2x_3^2+r_4^2x_4^2+2x_3x_4+2r_3x_3^2+2r_4x_4^2+2r_3x_3x_4$$
$$+2r_4x_3x_4+2r_3r_4x_3x_4\Big]x_3\,d\tau_3\,d\tau_4$$

and out of all the forty five integrals into which each of the above breaks. The non-zero ones are listed below.

The non-zero parts of the integral

$$\frac{4}{R^3}\iint e^{-2n(r_1+r_2)}(1+2c\,r_{12}+c^2r_{12}^2)\Big[1+2A(x_1+x_2+r_1x_1+r_2x_2)+A^2(x_1^2+x_2^2$$
$$+r_1^2x_1^2+r_2^2x_2^2+2x_1x_2+2r_1x_1^2+2r_2x_2^2+2r_1x_1x_2$$
$$+2r_2x_1x_2+2r_1r_2x_1x_2\Big]x_1\,d\tau_1\,d\tau_2$$

(1) $\dfrac{4\times 2A}{R^3}\iint x_1^2\,e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \dfrac{8\pi^2 A}{R^3 n^8} = \dfrac{F}{R^3}\times .2222$

(2) $\dfrac{4\times 2A}{R^3}\iint r_1 x_1^2\,e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \dfrac{20\pi^2 A}{R^3 n^9} = \dfrac{F}{R^3}\times .3004$

(3) $\dfrac{4\times 4Ac}{R^3}\iint x_1^2 r_{12}\,e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \dfrac{4\pi^2 Ac}{R^3 n^9}\times\dfrac{189}{16} = \dfrac{F}{R^3}\times .2583$

(4) $\dfrac{4\times 4Ac}{R^3}\iint r_{12}x_1^2 r_1\,e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \dfrac{4\pi^2 Ac}{R^3 n^{10}}\times\dfrac{2163}{64} = \dfrac{F}{R^3}\times .4002$

(5) $\dfrac{8Ac^2}{R^3}\iint r_{12}^2 x_1^2\,e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \dfrac{4\pi^2 Ac^2}{R^3 n^{10}}\times 21 = \dfrac{F}{R^3}\times .0904$

(6) $\dfrac{8Ac^2}{R^3}\iint r_{12}^2 r_1 x_1^2\,e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \dfrac{4\pi^2 Ac^2}{R^3 n^{11}}\times\dfrac{135}{2} = \dfrac{F}{R^3}\times .1572.$

While the non-zero parts of the second integral

$$\iint e^{-2n(r_3+r_4)}\left(1+2cr_{34}+c^2r_{34}^2\right)\Big[1-2A\left(x_3+x_4+r_3x_3+r_4x_4\right)+A^2\big(x_3^2+x_4^2+r_3^2x_3^2+r_4^2x_4^2+2x_3x_4+2r_3x_3^2+2r_4x_4^2+2r_3x_3x_4+2r_4x_3x_4+2r_3r_4x_3x_4\big)\Big]x_3\,d\tau_3\,d\tau_4$$

are

$$(1)\quad -2A\iint r_3^2\,e^{-2n(r_3+r_4)}\,d\tau_3\,d\tau_4 = -0\cdot[illegible]5\,F$$

$$(2)\quad -2A\iint r_3\,x_3^2\,e^{-2n(r_3+r_4)}\,d\tau_3\,d\tau_4 = -0\cdot0075\,F$$

$$(3)\quad -4Ac\iint r_{34}\,x_3^2\,e^{-2n(r_3+r_4)}\,d\tau_3\,d\tau_4 = -0\cdot0648\,F$$

$$(4)\quad -4Ac\iint r_{34}\,r_3\,x_3^2\,e^{-2n(r_3+r_4)}\,d\tau_3\,d\tau_4 = -0\cdot0992\,F$$

$$(5)\quad -2Ac^2\iint r_{34}^2\,x_3^2\,e^{-2n(r_3+r_4)}\,d\tau_3\,d\tau_4 = -0\cdot0226\,F$$

$$(6)\quad -2Ac^2\iint r_{34}^2\,r_3\,x_3^2\,e^{-2n(r_3+r_4)}\,d\tau_3\,d\tau_4 = -0\cdot0393\,F$$

The value of the integral

$$\iiiint \psi_1^2\,V\,\psi_2^2\,d\tau_1\,d\tau_2\,d\tau_3\,d\tau_4$$

is obtained from the above to be equal to

$$-\frac{F^2}{R^3}\times1\cdot4287\times\cdot2889 = -\frac{F^2}{R^3}\times\cdot4128$$

APPENDIX C

The integral $\iiiint \psi_1^2 V^2 \psi_2^2 \, d\tau_1 \, d\tau \, d\tau_3 \, d\tau_4$,

which enters in the second order interaction energy, is evaluated here. We have

$$\iiiint \psi_1^2 V^2 \psi_2^2 \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4$$

$$= \iiiint e^{-2n(r_1+r_2)} \left(1+2cr_{12}+c^2r_{12}^2\right)\Big[1+2A(x_1+x_2+r_1x_1+r_2x_2) + A^2(x_1^2+x_2^2+$$
$$r_1^2x_1^2 + r_2^2x_2^2 + 2x_1x_2 + 2r_1x_1^2 + 2r_2x_2^2 + 2r_1x_1x_2 + 2r_2x_1x_2$$
$$+ 2r_1r_2x_1x_2\Big] \times \frac{1}{R^6}\Big[\,(x_1^2x_3^2 + y_1^2y_3^2 + 4z_1^2z_3^2 + 2x_1x_3y_1y_3$$
$$-4x_1x_3z_1z_3 - 4y_1y_3z_1z_3) + \text{3 more terms of the same}$$
$$\text{type} \quad + 2(x_1x_3+y_1y_3-2z_1z_3)(x_1x_4+y_1y_4-2z_1z_4)$$
$$+ \text{5 more terms of this type}\Big] \times e^{-2n(r_3+r_4)}\left(1+2cr_{34}+c^2r_{34}^2\right)\Big[1-$$
$$2A(x_3+x_4+r_3x_3+r_4x_4) + A^2(x_3^2+x_4^2+r_3^2x_3^2+r_4^2x_4^2$$
$$+2x_3x_4 + 2r_3x_3^2 + 2r_4x_4^2 + 2r_3x_3x_4 + 2r_4x_3x_4$$
$$+2x_3x_4r_3r_4)\Big] \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4$$

$$= \Big\{\frac{1}{R^6}\iint e^{-2n(r_1+r_2)}\left(1+2cr_{12}+c^2r_{12}^2\right)\Big[1+2A(x_1+x_2+r_1x_1+r_2x_2)+A^2(x_1^2+x_2^2$$
$$+r_1^2x_1^2 + r_2^2x_2^2 + 2x_1x_2 + 2r_1x_1^2 + 2r_2x_2^2 + 2r_1x_1x_2$$
$$+2r_2x_1x_2 + 2r_1r_2x_1x_2)\Big] x_1^2 \, d\tau_1 \, d\tau_2 \times \iint e^{-2n(r_3+r_4)}\left(1+2cr_{34}+\right.$$
$$\left.c^2r_{34}\right)\Big[1-2A(x_3+x_4+r_3x_3+r_4x_4) + A^2(x_3^2+x_4^2+r_3^2x_3^2+r_4^2x_4^2$$
$$+2x_3x_4 + 2r_3x_3^2 + 2r_4x_4^2 + 2r_3x_3x_4 + 2r_4x_3x_4$$
$$+2r_3r_4x_3x_4\Big] x_3^2 \, d\tau_3 \, d\tau_4$$

$$+\frac{1}{R^6}\iint e^{-2n(r_1+r_2)}(1+2cr_{12}+c^2r_{12}^2)\Big[1+2A(x_1+x_2+r_1x_1+r_2x_2)+A^2(x_1^2+x_2^2$$

$$+r_1^2x_1^2+r_2^2x_2^2+2x_1x_2+2r_1x_1^2+2r_2x_2^2+2r_1x_1x_2$$

$$+2r_2x_1x_2+2r_1r_2x_1x_2)\Big]\,y_1^2\,d\tau_1\,d\tau_2\times\iint e^{-2n(r_3+r_4)}(1+2cr_{34}+$$

$$c^2r_{34}^2)\Big[1-2A(x_3+x_4+r_3x_3+r_4x_4)+A^2(x_3^2+x_4^2+r_3^2x_3^2$$

$$+r_4^2x_4^2+2x_3x_4+2r_3x_3^2+2r_4x_4^2+2r_3x_3x_4+2r_4x_3x_4$$

$$+2r_3r_4x_3x_4)\Big]\,y_3^2\,d\tau_3\,d\tau_4$$

$$+\frac{4}{R^6}\iint e^{-2n(r_1+r_2)}(1+2cr_{12}+c^2r_{12}^2)\Big[1+2A(x_1+x_2+r_1x_1+r_2x_2)+A^2(x_1^2$$

$$+x_2^2+r_1^2x_1^2+r_2^2x_2^2+2x_1x_2+2r_1x_1^2+2r_2x_2^2$$

$$+2r_1x_1x_2+2r_2x_1x_2+2r_1r_2x_1x_2)\Big]\,z_1^2\,d\tau_1\,d\tau_2$$

$$\times\iint e^{-2n(r_3+r_4)}(1+2cr_{34}+c^2r_{34}^2)\Big[1-2A(x_3+x_4+r_3x_3+r_4x_4)+A^2(x_3^2$$

$$+x_4^2+r_3^2x_3^2+r_4^2x_4^2+2x_3x_4+2r_3x_3^2+2r_4x_4^2+2r_3x_3x_4$$

$$+2r_4x_3x_4+2r_3r_4x_3x_4)\Big]\,z_3^2\,d\tau_3\,d\tau_4$$

$$+\frac{2}{R^6}\iint e^{-2n(r_1+r_2)}(1+2cr_{12}+c^2r_{12}^2)\Big[1+2A(x_1+x_2+r_1x_1+r_2x_2)+A^2(x_1^2+x_2^2$$

$$+r_1^2x_1^2+r_2^2x_2^2+2x_1x_2+2r_1x_1^2+2r_2x_2^2+2r_1x_1x_2$$

$$+2r_2x_1x_2+2r_1r_2x_1x_2)\Big]\,x_1y_1\,d\tau_1\,d\tau_2\times\iint e^{-2n(r_3+r_4)}(1+2cr_{34}+c^2r_{34}^2)$$

$$\Big[1-2A(x_3+x_4+r_3x_3+r_4x_4)+A^2(x_3^2+x_4^2+r_3^2x_3^2$$

$$+r_4^2x_4^2+2x_3x_4+2r_3x_3^2+2r_4x_4^2+2r_3x_3x_4$$

$$+2r_4x_3x_4+2r_3r_4x_3x_4)\Big]\,x_3y_3\,d\tau_3\,d\tau_4$$

$$
\begin{aligned}
-\frac{4}{R^6}\iint & e^{-2n(r_1+r_2)}(1+2cr_{12}+c^2r_{12}^2)\Big[1+2A(x_1+x_2+r_1x_1+r_2x_2)+A^2(x_1^2+\\
& x_2^2+r_1^2x_1^2+r_2^2x_2^2+2x_1x_2+2r_1x_1^2+2r_2x_2^2+2r_1x_1x_2\\
& +2r_2x_1x_2+2r_1r_2x_1x_2)\Big]\,x_1z_1\,d\tau_1\,d\tau_2 \times \iint e^{-2n(r_3+r_4)}(1+2cr_{34}+\\
& +c^2r_{34}^2)\Big[1-2A(x_3+x_4+r_3x_3+r_4x_4)+A^2(x_3^2+x_4^2+r_3^2x_3^2\\
& +r_4^2x_4^2+2x_3x_4+2r_3x_3^2+2r_4x_4^2+2r_3r_4x_3x_4\\
& +2r_3x_3x_4+2r_4x_3x_4)\Big]\,x_3z_3\,d\tau_3\,d\tau_4
\end{aligned}
$$

$$
\begin{aligned}
-\frac{4}{R^6}\iint & e^{-2n(r_1+r_2)}(1+2cr_{12}+c^2r_{12}^2)\Big[1+2A(x_1+x_2+r_1x_1+r_2x_2)+A^2(x_1^2\\
& +x_2^2+r_1^2x_1^2+r_2^2x_2^2+2x_1x_2+2r_1x_1^2+2r_2x_2^2\\
& +2r_1x_1x_2+2r_2x_1x_2+2r_1r_2x_1x_2)\Big]\,y_1z_1\,d\tau_1\,d\tau_2\\
\times\iint & e^{-2n(r_3+r_4)}(1+2cr_{34}+c^2r_{34}^2)\Big[1-2A(x_3+x_4+r_3x_3+r_4x_4)+A^2(x_3^2+x_4^2+\\
& r_3^2x_3^2+r_4^2x_4^2+2x_3x_4+2r_3x_3^2+2r_4x_4^2+2r_3x_3x_4\\
& +2r_4x_3x_4+2r_3r_4x_3x_4)\Big]\,y_3z_3\,d\tau_3\,d\tau_4\Bigg\}+3\text{ sets of}
\end{aligned}
$$

terms of the same type,

$$
\begin{aligned}
+\Bigg\{\frac{2}{R^6}\iint & e^{-2n(r_1+r_2)}(1+2cr_{12}+c^2r_{12}^2)\Big[1+2A(x_1+x_2+r_1x_1+r_2x_2)+A^2(x_1^2+x_2^2\\
& +r_1^2x_1^2+r_2^2x_2^2+2x_1x_2+2r_1x_1^2+2r_2x_2^2+2r_1x_1x_2\\
& +2r_2x_1x_2+2r_1r_2x_1x_2)\Big]\,x_1^2\,d\tau_1\,d\tau_2\times\iint e^{-2n(r_3+r_4)}(1+2cr_{34}+c^2r_{34}^2)\\
& \Big[1-2A(x_3+x_4+r_3x_3+r_4x_4)+A^2(x_3^2+x_4^2+r_3^2x_3^2+r_4^2x_4^2\\
& +2x_3x_4+2r_3x_3x_4+2r_4x_3x_4+2r_3x_3^2+2r_4x_4^2\\
& +2r_3r_4x_3x_4)\Big]\,x_3x_4\,d\tau_3\,d\tau_4
\end{aligned}
$$

$$+ \frac{2}{R^6} \iint e^{-2n(r_1+r_2)} (1 + 2c r_{12} + c^2 r_{12}^2) \Big[1 + 2A(x_1 + x_2 + r_1 x_1 + r_2 x_2) + A^2 (x_1^2 +$$

$$x_2^2 + r_1^2 x_1^2 + r_2^2 x_2^2 + 2x_1 x_2 + 2r_1 x_1^2 + 2 r_2 x_2^2 + 2 r_1 x_1 x_2$$

$$+ 2 r_2 x_1 x_2 + 2 r_1 r_2 x_1 x_2)\Big] x_1 y_1 \, d\tau_1 \, d\tau_2 \times \iint e^{-2n(r_3+r_4)} (1 + 2c r_{34} + c^2 r_{34}^2)$$

$$\Big[1 - 2A(x_3 + x_4 + r_3 x_3 + r_4 x_4) + A^2 (x_3^2 + x_4^2 + r_3^2 x_3^2 + r_4^2 x_4^2$$

$$+ 2 x_3 x_4 + 2 r_3 x_3 x_4 + 2 r_3 x_3^2 + 2 r_4 x_4^2 + 2 r_4 x_3 x_4$$

$$+ 2 r_3 r_4 x_3 x_4)\Big] x_3 y_4 \, d\tau_3 \, d\tau_4$$

$$- \frac{4}{R^6} \iint e^{-2n(r_1+r_2)} (1 + 2c r_{12} + c^2 r_{12}^2) \Big[1 + 2A(x_1 + x_2 + r_1 x_1 + r_2 x_2) + A^2 (x_1^2 + x_2^2$$

$$+ r_1^2 x_1^2 + r_2^2 x_2^2 + 2 x_1 x_2 + 2 r_1 x_1^2 + 2 r_2 x_2^2 + 2 r_1 x_1 x_2$$

$$+ 2 r_2 x_1 x_2 + 2 r_1 r_2 x_1 x_2)\Big] x_1 z_1 \, d\tau_1 \, d\tau_2 \times \iint e^{-2n(r_3+r_4)} (1 + 2c r_{34}$$

$$+ c^2 r_{34}^2) \Big[1 - 2A(x_3 + x_4 + r_3 x_3 + r_4 x_4) + A^2 (x_3^2 + x_4^2$$

$$+ r_3^2 x_3^2 + r_4^2 x_4^2 + 2 x_3 x_4 + 2 r_3 x_3^2 + 2 r_4 x_4^2 + 2 r_3 x_3 x_4$$

$$+ 2 r_4 x_3 x_4 + 2 r_3 r_4 x_3 x_4)\Big] x_3 z_4 \, d\tau_3 \, d\tau_4$$

$$+ \frac{2}{R^6} \iint e^{-2n(r_1+r_2)} (1 + 2c r_{12} + c^2 r_{12}^2) \Big[1 + 2A(x_1 + x_2 + r_1 x_1 + r_2 x_2) + A^2 (x_1^2 + x_2^2$$

$$+ r_1^2 x_1^2 + r_2^2 x_2^2 + 2 x_1 x_2 + 2 r_1 x_1^2 + 2 r_2 x_2^2 + 2 r_1 x_1 x_2$$

$$+ 2 r_2 x_1 x_2 + 2 r_1 r_2 x_1 x_2)\Big] y_1^2 \, d\tau_1 \, d\tau_2 \times \iint e^{-2n(r_3+r_4)} (1 + 2c r_{34} + c^2 r_{34}^2)$$

$$\Big[1 - 2A(x_3 + x_4 + r_3 x_3 + r_4 x_4) + A^2 (x_3^2 + x_4^2 + r_3^2 x_3^2$$

$$+ r_4^2 x_4^2 + 2 x_3 x_4 + 2 x_3^2 r_3 + 2 r_4 x_4^2 + 2 r_4 x_3 x_4$$

$$+ 2 r_3 x_3 x_4 + 2 r_3 r_4 x_3 x_4)\Big] y_3 y_4 \, d\tau_3 \, d\tau_4$$

$$- \frac{4}{R^6} \iint e^{-2n(r_1+r_2)} (1 + 2c r_{12} + c^2 r_{12}^2) \Big[1 + 2A(x_1 + x_2 + r_1 x_1 + r_2 x_2) + A^2 (x_1^2 +$$

$$+ x_2^2 + r_1^2 x_1^2 + r_2^2 x_2^2 + 2x_1x_2 + 2r_1x_1^2 + 2r_2x_2^2 + 2r_1x_1x_2$$

$$+ 2r_2x_1x_2 + 2r_1r_2x_1x_2)\Big]\, y_1 z_1 \, d\tau_1 \, d\tau_2 \times \iint e^{-2n(r_3+r_4)} (1 + 2cr_{34} + c^2 r_{34}^2)$$

$$\Big[1 - 2A(x_3 + x_4 + r_3x_3 + r_4x_4) + A^2(x_3^2 + x_4^2 + r_3^2x_3^2 + r_4^2x_4^2$$

$$+ 2x_3x_4 + 2r_3x_3^2 + 2r_4x_4^2 + 2r_3x_3x_4 + 2r_4x_3x_4$$

$$+ 2r_3r_4x_3x_4)\Big]\, y_3 z_4 \, d\tau_3 \, d\tau_4$$

$$- \frac{4}{R^6} \iint e^{-2n(r_1+r_2)} (1 + 2cr_{12} + c^2r_{12}^2)\Big[1 + 2A(x_1 + x_2 + r_1x_1 + r_2x_2) + A^2(x_1^2 + x_2^2 +$$

$$r_1^2x_1^2 + r_2^2x_2^2 + 2x_1x_2 + 2r_1x_1^2 + 2r_2x_2^2 + 2r_1x_1x_2 + 2r_2x_1x_2$$

$$+ 2r_1r_2x_1x_2)\Big]\, x_1 z_1 \, d\tau_1 \, d\tau_2 \times \iint e^{-2n(r_3+r_4)} (1 + 2cr_{34} + c^2r_{34}^2)\Big[1 - 2A(x_3 +$$

$$x_4 + r_3x_3 + r_4x_4) + A^2(x_3^2 + x_4^2 + r_3^2x_3^2 + r_4^2x_4^2 + 2x_3x_4$$

$$+ 2r_3x_3^2 + 2r_4x_4^2 + 2r_3x_3x_4 + 2r_4x_3x_4 + 2r_3r_4x_3x_4)\Big]\, x_4 z_3 \, d\tau_3 \, d\tau_4$$

$$- \frac{4}{R^6} \iint e^{-2n(r_1+r_2)} (1 + 2cr_{12} + c^2r_{12}^2)\Big[1 + 2A(x_1 + x_2 + r_1x_1 + r_2x_2) + A^2(x_1^2 + x_2^2$$

$$+ r_1^2x_1^2 + r_2^2x_2^2 + 2x_1x_2 + 2r_1x_1^2 + 2r_2x_2^2 + 2r_1x_1x_2$$

$$+ 2r_2x_1x_2 + 2r_1r_2x_1x_2)\Big]\, y_1 z_1 \, d\tau_1 \, d\tau_2 \times \iint e^{-2n(r_3+r_4)} (1 + 2cr_{34} + c^2r_{34}^2)\Big[1 -$$

$$2A(x_3 + x_4 + r_3x_3 + r_4x_4) + A^2(x_3^2 + x_4^2 + r_3^2x_3^2 + r_4^2x_4^2 + 2x_3x_4$$

$$+ 2r_3x_3^2 + 2r_4x_4^2 + 2r_3x_3x_4 + 2r_4x_3x_4 + 2r_3r_4x_3x_4)\Big]\, y_4 z_3 \, d\tau_3 \, d\tau_4$$

$$+ \frac{8}{R^6} \iint e^{-2n(r_1+r_2)} (1 + 2cr_{12} + c^2r_{12}^2)\Big[1 + 2A(x_1 + x_2 + r_1x_1 + r_2x_2) + A^2(x_1^2 + x_2^2 +$$

$$r_1^2x_1^2 + r_2^2x_2^2 + 2x_1x_2 + 2r_1x_1^2 + 2r_2x_2^2 + 2r_1x_1x_2 + 2r_2x_1x_2$$

$$+ 2r_1r_2x_1x_2)\Big]\, z_1^2 \, d\tau_1 \, d\tau_2 \times \iint e^{-2n(r_3+r_4)} (1 + 2cr_{34} + c^2r_{34}^2)\Big[1 - 2A(x_3 + x_4$$

$$+ r_3x_3 + r_4x_4) + A^2(x_3^2 + x_4^2 + r_3^2x_3^2 + r_4^2x_4^2 + 2x_3x_4 + 2r_3x_3^2$$

$$+ 2r_4x_4^2 + 2r_3x_3x_4 + 2r_4x_3x_4 + 2r_3r_4x_3x_4)\Big]\, z_3 z_4 \, d\tau_3 \, d\tau_4$$

$$+ \frac{2}{R^6} \iint e^{-2n(r_1+r_2)} (1+2cr_{12}+c^2r_{12}^2) \Big[1 + 2A(x_1+x_2+r_1x_1+r_2x_2) + A^2(x_1^2+x_2^2$$

$$+ r_1^2x_1^2 + r_2^2x_2^2 + 2x_1x_2 + 2r_1x_1^2 + 2r_2x_2^2 + 2r_1x_1x_2 + 2r_2x_1x_2$$

$$+ 2r_1r_2x_1x_2)\Big] x_1 y_1 \, d\tau_1 \, d\tau_2 \times \iint e^{-2n(r_3+r_4)} (1+2cr_{34}+c^2r_{34}^2) \Big[1 - 2A(x_3$$

$$+ x_4 + r_3x_3 + r_4x_4) + A^2(x_3^2 + x_4^2 + r_3^2x_3^2 + r_4^2x_4^2 + 2x_3x_4$$

$$+ 2r_3x_3^2 + 2r_4x_4^2 + 2r_3x_3x_4 + 2r_4x_3x_4 + 2r_3r_4x_3x_4)\Big] y_3 x_4 \, d\tau_3 \, d\tau_4 \Big\}$$

+ five more terms of the same type.

It is easy to notice that each integral of the first three terms of the first set has same value on account of symmetry. The remaining ones are zero. Thus, we list below the non-zero integrals into which the first integrals of the first three terms of the first set break. They are

$$\text{(A)} \quad (1) \quad \frac{1}{R^6} \iint x_1^2 \, e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = \frac{\pi^2}{R^6 n^8} = \frac{.0722}{R^6}$$

$$(2) \quad \frac{A^2}{R^6} \iint x_1^4 \, e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = \frac{9\pi^2 A^2}{2R^6 n^{10}} = \frac{.0141F^2}{R^6}$$

$$(3) \quad \frac{A^2}{R^6} \iint x_1^2 x_2^2 \, e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = \frac{\pi^2 A^2}{R^6 n^{10}} = \frac{.0031F^2}{R^6}$$

$$(4) \quad \frac{A^2}{R^6} \iint r_1^2 x_1^4 \, e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = \frac{63\pi^2 A^2}{R^6 n^{12}} = \frac{.0576F^2}{R^6}$$

$$(5) \quad \frac{A^2}{R^6} \iint x_1^2 x_2^2 r_2^2 \, e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = \frac{15\pi^2 A^2}{2R^6 n^{12}} = \frac{.0069F^2}{R^6}$$

$$(6) \quad \frac{2A^2}{R^6} \iint r_1 x_1^4 \, e^{-2n(r_1+r_2)} \, d\tau_1 \, d\tau_2 = \frac{63\pi^2 A^2}{2R^6 n^{12}} = \frac{.0532F^2}{R^6}$$

(7) $$\frac{2A^2}{R^6}\iint r_2\, x_1^2 x_2^2 e^{-2n(r_1+r_2)}\, dr_1\, dr_2 = \frac{5\pi^2 A^2}{R^6 n^{11}} = \frac{.0085\,F^2}{R^6}$$

(8) $$\frac{2c}{R^6}\iint r_{12}\, x_1^2\, e^{-2n(r_1+r_2)}\, dr_1\, dr_2 = \frac{189\,\pi^2 c}{32\,R^6 n^9} = \frac{.0840}{R^6}$$

(9) $$\frac{2A^2c}{R^6}\iint r_{12}\, x_1^4\, e^{-2n(r_1+r_2)}\, dr_1\, dr_2 = \frac{\pi^2 A^2 c}{R^6 n^{11}} \times \frac{8775}{256} = \frac{.0211\,F^2}{R^6}$$

(10) $$\frac{2A^2c}{R^6}\iint r_{12}\, x_1^2 x_2^2\, e^{-2n(r_1+r_2)}\, dr_1\, dr_2 = \frac{\pi^2 A^2 c}{R^6 n^{11}} \times \frac{1975}{256} = \frac{.0047\,F^2}{R^6}$$

(11) $$\frac{2A^2c}{R^6}\iint r_{12}\, r_1^2 x_1^4\, e^{-2n(r_1+r_2)}\, dr_1\, dr_2 = \frac{\pi^2 A^2 c}{R^6 n^{13}} \times \frac{2431\times 21}{256} = \frac{.0358\,F^2}{R^6}$$

(12) $$\frac{2A^2c}{R^6}\iint r_{12} r_2^2\, x_1^2 x_2^2\, e^{-2n(r_1+r_2)}\, dr_1\, dr_2 = \frac{\pi^2 A^2 c}{R^6 n^{13}} \times \frac{8275}{128} = \frac{.0116\,F^2}{R^6}$$

(13) $$\frac{4A^2c}{R^6}\iint r_{12}\, r_1\, x_1^4\, e^{-2n(r_1+r_4)}\, dr_1\, dr_2 = \frac{\pi^2 A^2 c}{R^6 n^{12}} \times \frac{9\times 15345}{512} = \frac{.0897\,F^2}{R^6}$$

(14) $$\frac{4A^2c}{R^6}\iint r_{12}\, r_2\, x_1^2 x_2^2\, e^{-2n(r_1+r_4)}\, dr_1\, dr_2 = \frac{\pi^2 A^2 c}{R^6 n^{12}} \times \frac{19965}{512} = \frac{.0129\,F^2}{R^6}$$

(15) $$\frac{c^2}{R^6}\iint r_{12}^2\, x_1^2\, e^{-2n(r_1+r_2)}\, dr_1\, dr_2 = \frac{\pi^2 c^2}{R^6 n^{10}} \times \frac{21}{2} = \frac{.0294}{R^6}$$

(16) $$\frac{A^2c^2}{R^6}\iint r_{12}^2\, x_1^4\, e^{-2n(r_1+r_2)}\, dr_1\, dr_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{12}} \times \frac{153}{2} = \frac{.0092\,F^2}{R^6}$$

(17) $$\frac{A^2c^2}{R^6}\iint r_{12}^2\, x_1^2 x_2^2\, e^{-2n(r_1+r_2)}\, dr_1\, dr_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{12}} \times 15 = \frac{.0018\,F^2}{R^6}$$

(18) $$\frac{A^2c^2}{R^6}\iint r_{12}^2\, r_1^2\, x_1^4\, e^{-2n(r_1+r_2)}\, dr_1\, dr_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{14}} \times \frac{3213}{2} = \frac{.0569\,F^2}{R^6}$$

(19) $$\frac{A^2c^2}{R^6}\iint r_{12}^2\, r_2^2\, x_1^2 x_2^2\, e^{-2n(r_1+r_2)}\, dr_1\, dr_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{14}} \times \frac{645}{4} = \frac{.0057\,F^2}{R^6}$$

(20) $$\frac{2A^2c^2}{R^6}\iint r_{12}^2\, r_1\, x_1^4\, e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2A^2c^2}{R^6n^{13}}\times\frac{1323}{2} = \frac{.0433\,F^2}{R^6}$$

(21) $$\frac{2A^2c^2}{R^6}\iint r_{12}^2\, r_2\, x_1^2\, x_2^2\, e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2A^2c^2}{R^6n^{13}}\times 90 = \frac{.0059\,F^2}{R^6}$$

(B)

(1) $$\frac{1}{R^6}\iint y_1^2\, e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2}{R^6n^8} = \frac{.0722}{R^6}$$

(2) $$\frac{A^2}{R^6}\iint x_1^2\, y_1^2\, e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2A^2}{R^6n^{10}}\times\frac{3}{2} = \frac{.0047\,F^2}{R^6}$$

(3) $$\frac{A^2}{R^6}\iint x_2^2\, y_1^2\, e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2A^2}{R^6n^{10}} = \frac{.0031\,F^2}{R^6}$$

(4) $$\frac{A^2}{R^6}\iint r_1^2\, x_1^2\, y_1^2\, e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2A^2}{R^6n^{12}}\times 21 = \frac{.0192\,F^2}{R^6}$$

(5) $$\frac{A^2}{R^6}\iint r_2^2\, x_2^2\, y_1^2\, e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2A^2}{R^6n^{12}}\times\frac{15}{2} = \frac{.0069\,F^2}{R^6}$$

(6) $$\frac{2A^2}{R^6}\iint r_1\, x_1^2\, y_1^2\, e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2A^2}{R^6n^{11}}\times\frac{21}{2} = \frac{.0177\,F^2}{R^6}$$

(7) $$\frac{2A^2}{R^6}\iint r_2\, x_2^2\, y_1^2\, e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2A^2}{R^6n^{11}}\times 5 = \frac{.0085\,F^2}{R^6}$$

(8) $$\frac{2c}{R^6}\iint r_{12}\, y_1^2\, e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2c}{R^6n^9}\times\frac{189}{32} = \frac{.0840}{R^6}$$

(9) $$\frac{2A^2c}{R^6}\iint r_{12}\, x_1^2\, y_1^2\, e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2A^2c}{R^6n^{11}}\times\frac{2925}{256} = \frac{.0070\,F^2}{R^6}$$

(10) $$\frac{2A^2c}{R^6}\iint r_{12}\, x_2^2\, y_1^2\, e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2A^2c}{R^6n^{11}}\times\frac{1975}{256} = \frac{.0047\,F^2}{R^6}$$

(11) $\frac{2A^2c}{R^6}\iint r_{12}\, r_1^2\, x_1^2\, y_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c}{R^6 n^{13}} \times \frac{2431\times 7}{256} = \frac{.0119F^2}{R^6}$

(12) $\frac{2A^2c}{R^6}\iint r_{12}\, r_2^2\, x_2^2\, y_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c}{R^6 n^{13}} \times \frac{8275}{128} = \frac{.0116F^2}{R^6}$

(13) $\frac{4A^2c}{R^6}\iint r_{12}\, r_1\, x_1^2 y_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c}{R^6 n^{12}} \times \frac{3\times 15345}{512} = \frac{.0299F^2}{R^6}$

(14) $\frac{4A^2c}{R^6}\iint r_{12}\, r_2\, x_2^2\, y_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c}{R^6 n^{12}} \times \frac{19965}{512} = \frac{.0129F^2}{R^6}$

(15) $\frac{c^2}{R^6}\iint r_{12}^2\, y_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 c^2}{R^6 n^{10}} \times \frac{21}{2} = \frac{.0294}{R^6}$

(16) $\frac{A^2c^2}{R^6}\iint r_{12}^2\, x_1^2\, y_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{12}} \times \frac{51}{2} = \frac{.0031F^2}{R^6}$

(17) $\frac{A^2c^2}{R^6}\iint r_{12}^2\, x_2^2\, y_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{12}} \times 15 = \frac{.0018F^2}{R^6}$

(18) $\frac{A^2c^2}{R^6}\iint r_1^2\, r_{12}^2\, x_1^2\, y_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{14}} \times \frac{1071}{2} = \frac{.0189F^2}{R^6}$

(19) $\frac{A^2c^2}{R^6}\iint r_{12}^2\, r_2^2\, x_2^2\, y_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{14}} \times \frac{645}{4} = \frac{.0057F^2}{R^6}$

(20) $\frac{2A^2c^2}{R^6}\iint r_{12}^2\, r_1\, x_1^2\, y_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{13}} \times \frac{441}{2} = \frac{.0144F^2}{R^6}$

(21) $\frac{2A^2c^2}{R^6}\iint r_{12}^2\, r_2\, x_2^2\, y_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{13}} \times 90 = \frac{.0059F^2}{R^6}$

(e) (1) $\frac{1}{R^6}\iint z_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2}{R^6 n^8} = \frac{.0722}{R^6}$

(2) $$\frac{A^2}{R^6}\iint x_1^2 z_1^2 e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{3\pi^2 A^2}{2R^6 n^{10}} = \frac{.0047F^2}{R^6}$$

(3) $$\frac{A^2}{R^6}\iint x_2^2 z_1^2 e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2 A^2}{R^6 n^{10}} = \frac{.0031F^2}{R^6}$$

(4) $$\frac{A^2}{R^6}\iint r_1^2 x_1^2 z_1^2 e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2 A^2}{R^6 n^{12}} \times 21 = \frac{.0192F^2}{R^6}$$

(5) $$\frac{A^2}{R^6}\iint r_2^2 x_2^2 z_1^2 e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2 A^2}{R^6 n^{12}} \times \frac{15}{2} = \frac{.0069F^2}{R^6}$$

(6) $$\frac{2A^2}{R^6}\iint r_1 x_1^2 z_1^2 e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2 A^2}{R^6 n^{11}} \times \frac{21}{2} = \frac{.0177F^2}{R^6}$$

(7) $$\frac{2A^2}{R^6}\iint r_2 x_2^2 z_1^2 e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2 A^2}{R^6 n^{11}} \times 5 = \frac{.0085F^2}{R^6}$$

(8) $$\frac{2c}{R^6}\iint r_{12} z_1^2 e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2 c}{R^6 n^9} \times \frac{189}{32} = \frac{.0840}{R^6}$$

(9) $$\frac{2A^2c}{R^6}\iint r_{12} x_1^2 z_1^2 e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2 A^2 c}{R^6 n^{11}} \times \frac{2925}{256} = \frac{.007F^2}{R^6}$$

(10) $$\frac{2A^2c}{R^6}\iint r_{12} x_2^2 z_1^2 e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2 A^2 c}{R^6 n^{11}} \times \frac{1975}{256} = \frac{.0047F^2}{R^6}$$

(11) $$\frac{2A^2c}{R^6}\iint r_{12} r_1^2 x_1^2 z_1^2 e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{7\pi^2 A^2 c}{R^6 n^{13}} \times \frac{2431}{256} = \frac{.0119F^2}{R^6}$$

(12) $$\frac{2A^2c}{R^6}\iint r_{12} r_2^2 x_2^2 z_1^2 e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2 A^2 c}{R^6 n^{13}} \times \frac{8275}{128} = \frac{.0116F^2}{R^6}$$

(13) $$\frac{4A^2c}{R^6}\iint r_{12} r_1 x_1^2 z_1^2 e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{3\pi^2 A^2 c}{R^6 n^{12}} \times \frac{15345}{512} = \frac{.0299F^2}{R^6}$$

(14) $$\frac{4A^2c}{R^6}\iint r_{12} r_2 x_2^2 z_1^2 e^{-2n(r_1+r_2)}\,d\tau_1\,d\tau_2 = \frac{\pi^2 A^2 c}{R^6 n^{12}} \times \frac{19965}{512} = \frac{.0129F^2}{R^6}$$

$$(15)\quad \frac{c^2}{R^6}\iint r_{12}^{2}\, z_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 c^2}{R^6 n^{10}}\times\frac{21}{2} = \frac{.0294\,F^2}{R^6}$$

$$(16)\quad \frac{A^2c^2}{R^6}\iint r_{12}^{-2}\, x_1^2\, z_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{12}}\times\frac{51}{2} = \frac{.0031\,F^2}{R^6}$$

$$(17)\quad \frac{A^2c^2}{R^6}\iint r_{12}^{-2}\, x_2^2\, z_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{12}}\times 15 = \frac{.0018\,F^2}{R^6}$$

$$(18)\quad \frac{A^2c^2}{R^6}\iint r_{12}^{2}\, r_1^{2}\, x_1^2\, z_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{14}}\times\frac{1071}{2} = \frac{.0189\,F^2}{R^6}$$

$$(19)\quad \frac{A^2c^2}{R^6}\iint r_{12}^{2}\, r_2^{2}\, x_2^2\, z_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 C^2}{R^6 n^{14}}\times\frac{645}{4} = \frac{.0057\,F^2}{R^6}$$

$$(20)\quad \frac{2A^2c^2}{R^6}\iint r_{12}^{2}\, r_1\, x_1^2\, z_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{13}}\times\frac{441}{2} = \frac{.0144\,F^2}{R^6}$$

$$(21)\quad \frac{2A^2c^2}{R^6}\iint r_{12}^{2}\, r_2\, x_2^2\, z_1^2\, e^{-2n(r_1+r_2)}\, d\tau_1\, d\tau_2 = \frac{\pi^2 A^2 c^2}{R^6 n^{13}}\times 90 = \frac{.0059\,F^2}{R^6}$$

Adding up each set (A), (B) and (C) we have the value of the first set of integrals

$$\frac{4}{R^6}\left[(\cdot1856+\cdot4420\,F^2)^2+(\cdot1856+\cdot1879\,F^2)^2+4(\cdot1856+\cdot1879\,F^2)^2\right]$$

$$=\frac{4}{R^6}\left[\cdot2064+\cdot5126\,F^2+\cdot3719\,F^4\right]$$

$$=\frac{1}{R^6}\left[\cdot8256+2\cdot504\,F^2+1\cdot487\,F^4\right]$$

Now we find out the value of the non-zero part of the second set of 6 integrals, one of whose representative is

$$\frac{2}{R^6}\iint e^{-2n(r_1+r_2)}\left(1+2cr_{12}+c^2r_{12}^2\right)\Big[1+2A(x_1+x_2+r_1x_1+r_2x_2)+A^2(x_1^2+x_2^2+r_1^2x_1^2+r_2^2x_2^2+2x_1x_2+2r_1x_1^2+2r_2x_2^2+2r_1x_1x_2+2r_2x_1x_2+2r_1r_2x_1x_2)\Big]x_1^2\,d\tau_1\,d\tau_2 \times \iint e^{-2n(r_3+r_4)}\left(1+2cr_{34}+c^2r_{34}^2\right)\Big[1-2A(x_3+x_4+r_3x_3+r_4x_4)+A^2(x_3^2+x_4^2+r_3^2x_3^2+r_4^2x_4^2+2x_3x_4+2r_3x_3^2+2r_4x_4^2+2r_3x_3x_4+2r_4x_3x_4+2r_3r_4x_3x_4)\Big]x_3x_4\,d\tau_3\,d\tau_4$$

As evaluated before the first integral has a value $\frac{2}{R^6}(.1856+.4420\,F^2)$ and the second has the following non-zero integrals

(1) $$2A^2\iint x_3^2x_4^2\,e^{-2n(r_3+r_4)}\,d\tau_3\,d\tau_4 = \frac{2\pi^2A^2}{n^{10}} = .0062\,F^2$$

(2) $$2A^2\iint r_3\,x_3^2x_4^2\,e^{-2n(r_3+r_4)}\,d\tau_3\,d\tau_4 = \frac{5\pi^2A^2}{n^{11}} = .0170\,F^2$$

(3) $$2A^2\iint r_4\,x_4^2x_3^2\,e^{-2n(r_3+r_4)}\,d\tau_3\,d\tau_4 = \frac{5\pi^2A^2}{n^{11}} = .0170\,F^2$$

(4) $$2A^2\iint r_3r_4\,x_3^2x_4^2\,e^{-2n(r_3+r_4)}\,d\tau_3\,d\tau_4 = \frac{25\pi^2A^2}{2n^{12}} = .0114\,F^2$$

(5) $$4A^2c\iint r_{34}\,x_3^2x_4^2\,e^{-2n(r_3+r_4)}\,d\tau_3\,d\tau_4 = \frac{\pi^2A^2c}{n^{11}}\times\frac{1975}{128} = .0094\,F^2$$

(6) $$4A^2c\iint r_{34}\,r_3\,x_3^2x_4^2\,e^{-2n(r_3+r_4)}\,d\tau_3\,d\tau_4 = \frac{\pi^2A^2c}{n^{12}}\times\frac{19965}{512} = .0129\,F^2$$

$$(7) \quad 4A^2c \iint r_{34}\, r_4\, x_3^2\, x_4^2\, e^{-2n(r_3+r_4)}\, d\tau_3\, d\tau_4 = \frac{\pi^2 A^2 c}{n^{12}} \times \frac{19965}{512} = \cdot 0129\, F^2$$

$$(8) \quad 4A^2c \iint r_{34}\, r_3 r_4\, x_3^2 x_4^2\, e^{-2n(r_3+r_4)}\, d\tau_3\, d\tau_4 = \frac{15\pi^2 A^2 c}{n^{13}} \times \frac{5401}{256} = \cdot 0189\, F^2$$

$$(9) \quad 2A^2c^2 \iint r_{34}^2\, x_3^2\, x_4^2\, e^{-2n(r_3+r_4)}\, d\tau_3\, d\tau_4 = \frac{\pi^2 A^2 c^2}{n^{12}} \times 30 = \cdot 0036\, F^2$$

$$(10) \quad 2A^2c^2 \iint r_{34}^2\, r_3\, x_3^2 x_4^2\, e^{-2n(r_3+r_4)}\, d\tau_3\, d\tau_4 = \frac{\pi^2 A^2 c^2}{n^{13}} \times 180 = \cdot 0118\, F^2$$

$$(11) \quad 2A^2c^2 \iint r_{34}^2\, r_4\, x_3^2\, x_4^2\, e^{-2n(r_3+r_4)}\, d\tau_3\, d\tau_4 = \frac{\pi^2 A^2 c^2}{n^{13}} \times 180 = \cdot 0118\, F^2$$

$$(12) \quad 2A^2c^2 \iint r_{34}^2\, r_3 r_4\, x_3^2 x_4^2\, e^{-2n(r_3+r_4)}\, d\tau_3\, d\tau_4 = \frac{\pi^2 A^2 c^2}{n^{14}} \times \frac{525}{2} = \cdot 0049\, F^2$$

The sum of these integrals has a value $.1378\ F^2$ and so the value of the second set of integrals is

$$6\left[\frac{2}{R^6}\left(\cdot 1856 + \cdot 4420\, F^2\right) \times \cdot 1378\, F^2\right]$$

$$= \frac{1}{R^6}\left[\cdot 3070\, F^2 + \cdot 7311\, F^4\right]$$

and finally the integral

$$\iiiint \psi_1^2 V^2 \psi_2^2\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{1}{R^6}\left[\cdot 8256 + 2\cdot 8110\, F^2 + 2\cdot 2181\, F^4\right]$$

APPENDIX D

First Order Interaction with Symmetrized Wave Functions

If we take into account the overlapping of electron wave functions of the two atoms we can write the total wave function of the system in any of the four ways

$$\psi_1(1,2)\ \psi_2(3,4)$$
$$\psi_1(1,4)\ \psi_2(2,3)$$
$$\psi_1(2,3)\ \psi_2(1,4)$$
$$\psi_1(3,4)\ \psi_2(1,2)$$

We have excluded in the above wave functions like $\psi_1(1,3)\ \psi_2(2,4)$ and $\psi_1(2,4)\ \psi_2(1,3)$ because of the operation of Pauli principle. The electrons 1 and 3 have spin in one direction and electrons 2 and 4 in opposite. So we do not exchange 1 and 4 or 2 and 3. We thus have a combination of four allowed wave functions which are antisymmetric in the electron coordinates 1 and 3, and also in 2 and 4

$$\psi = \psi_1(1,2)\psi_2(3,4) - \psi_1(1,4)\psi_2(2,3) - \psi_1(2,3)\psi_2(1,4) + \psi_1(3,4)\psi_2(1,2)$$

Making use of this we can write the first order interaction energy as

$$\Delta E_1 = \frac{\int V \psi^2 d\tau}{\int \psi^2 d\tau}$$

and

$$V = \frac{1}{R^3}\Big[(x_1x_3 + y_1y_3 - 2z_1z_3) + (x_1x_4 + y_1y_4 - 2z_1z_4) + (x_2x_3 + y_2y_3 - 2z_2z_3) + (x_2x_4 + y_2y_4 - 2z_2z_4)\Big]$$

Now the denominator in the expression for ΔE_1 is the integral $\int \psi^2 d\tau$

$$= \int\Big[\psi_1(1,2)\psi_2(3,4) - \psi_1(1,4)\psi_2(2,3) - \psi_1(2,3)\psi_2(1,4) + \psi_1(3,4)\psi_2(1,2)\Big]^2 d\tau$$

$$= \int \psi_1^2(1,2)\,\psi_2^2(3,4)\,d\tau + \int \psi_1^2(1,4)\,\psi_2^2(2,3)\,d\tau$$

$$+ \int \psi_1^2(2,3)\,\psi_2^2(1,4)\,d\tau + \int \psi_1^2(3,4)\,\psi_2^2(1,2)\,d\tau$$

$$-2\int \psi_1(1,2)\,\psi_2(3,4)\,\psi_1(1,4)\,\psi_2(2,3)\,d\tau - 2\int \psi_1(1,2)\,\psi_2(3,4)\,\psi_1(2,3)\,\psi_2(1,4)\,d\tau$$

$$+2\int \psi_1(1,2)\,\psi_2(3,4)\,\psi_1(3,4)\,\psi_2(1,2)\,d\tau + 2\int \psi_1(1,4)\,\psi_2(2,3)\,\psi_1(2,3)\,\psi_2(1,4)\,d\tau$$

$$-2\int \psi_1(2,3)\,\psi_2(1,4)\,\psi_1(3,4)\,\psi_2(1,2)\,d\tau - 2\int \psi_1(1,4)\,\psi_2(2,3)\,\psi_1(3,4)\,\psi_2(1,2)\,d\tau$$

and in this the first four terms have the same value and all the negative terms have the same value. The positive integrals having exchange terms are negligible because the terms such as $\psi_1(1,2)\,\psi_2(1,2)\,\psi_1(3,4)\,\psi_2(3,4)$ are very small due to the fact that it is highly improbable that electrons 1,2 or 3,4 will be associated with both the atoms at the same time. Thus we can write

$$\int \psi^2\,d\tau = 4I_1 - 8I_2$$

where typical I_1 and I_2 are

$$I_1 = \int \psi_1^2(1,2)\,\psi_2^2(3,4)\,d\tau$$

$$I_2 = \int \psi_1(1,2)\,\psi_2(3,4)\,\psi_1(1,4)\,\psi_2(2,3)\,d\tau$$

In the similar manner we can write the integral $\int V\psi^2 d\tau$ as

$$\frac{1}{R^3}\int\Big[(x_1x_3+y_1y_3-2z_1z_3)+(x_1x_4+y_1y_4-2z_1z_4)+(x_2x_3+y_2y_3-2z_2z_3)$$
$$+(x_2x_4+y_2y_4-2z_2z_4)\Big]\times\Big\{\psi_1^2(1,2)\,\psi_2^2(3,4)+\psi_1^2(1,4)\,\psi_2^2(2,3)$$
$$+\psi_1^2(2,3)\,\psi_2^2(1,4)+\psi_1^2(3,4)\,\psi_2^2(1,2)-2\psi_1(1,2)\,\psi_2(3,4)\,\psi_1(1,4)\,\psi_2(2,3)$$
$$-2\psi_1(1,2)\,\psi_2(3,4)\,\psi_1(2,3)\,\psi_2(1,4)+2\psi_1(1,2)\,\psi_2(3,4)\,\psi_1(3,4)\,\psi_2(1,2)$$
$$+2\psi_1(1,4)\,\psi_2(2,3)\,\psi_1(2,3)\,\psi_2(1,4)-2\psi_1(2,3)\,\psi_2(1,4)\,\psi_1(3,4)\,\psi_2(1,2)$$
$$-2\psi_1(1,4)\,\psi_2(2,3)\,\psi_1(3,4)\,\psi_2(1,2)\Big\}\,d\tau$$

which can also be written, after neglecting the parts mentioned on the last page, as

$$\frac{1}{R^3}\Big[4H_1-8H_2\Big]$$ where a typical

$$H_1=\int\Big[(x_1x_3+y_1y_3-2z_1z_3)+(x_1x_4+y_1y_4-2z_1z_4)+(x_2x_3+y_2y_3-2z_2z_3)$$
$$+(x_2x_4+y_2y_4-2z_2z_4)\Big]\psi_1^2(1,2)\,\psi_2^2(3,4)\,d\tau$$

and a typical H_2 is

$$H_2=\int\Big[(x_1x_3+y_1y_3-2z_1z_3)+(x_2x_3+y_2y_3-2z_2z_3)+(x_1x_4+y_1y_4-2z_1z_4)$$
$$+(x_2x_4+y_2y_4-2z_2z_4)\Big]\psi_1(1,2)\,\psi_2(3,4)\,\psi_1(1,4)\,\psi_2(2,3)\,d\tau$$

Hence

$$\Delta E_1=\frac{1}{R^3}\times\frac{H_1-2H_2}{I_1-2I_2}$$

We have already evaluated the values of the integrals I_1 and H_1 which are

$$I_1=(\cdot 2671+\cdot 3606\,F^2+\cdot 1216\,F^4)$$

and

$$H_1=-F^2\times\cdot 4128$$

So we proceed to evaluate the integrals I_2 and H_2 which as we see are exchange integrals.

$$I_2 = \int \psi_1(1,2)\,\psi_2(3,4)\,\psi_1(1,4)\,\psi_2(2,3)\,d\tau$$

$$= \iiiint \Big[e^{-n(r_1+r_2)} (1+cr_{12}) \left\{ 1 + A(x_1+x_2+r_1x_1+r_2x_2) \right\} e^{-n(r_3+r_4)} (1+cr_{34}) \left\{ 1 - A(x_3+x_4+ r_3x_3 + r_4x_4) \right\} e^{-n(r_1+r_4)} (1+cr_{14}) \left\{ 1 + A(x_1+x_4+r_1x_1+r_4x_4) \right\} e^{-n(r_2+r_3)} (1+cr_{23}) \left\{ 1 - A(x_2+x_3+r_2x_2+r_3x_3) \right\} \Big]\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4$$

$$= \iiiint e^{-2n(r_1+r_2+r_3+r_4)} (1+cr_{12})(1+cr_{34})(1+cr_{14})(1+cr_{23}) \left\{ 1 + A(x_1+x_2+r_1x_1+r_2x_2) \right\} \left\{ 1 - A(x_3+x_4+r_3x_3+r_4x_4) \right\} \left\{ 1 + A(x_1+x_4+r_1x_1+r_4x_4) \right\} \left\{ 1 - A(x_2+x_3+r_2x_2+r_3x_3) \right\} d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4$$

$$= \iiiint \Big[e^{-2n(r_1+r_2+r_3+r_4)} \big[1 + c(r_{12}+r_{34}+r_{14}+r_{23}) + c^2(r_{12}r_{34} + r_{12}r_{14} + r_{12}r_{23} + r_{34}r_{14} + r_{34}r_{23} + r_{14}r_{23}) + c^3(r_{12}r_{34}r_{14} + r_{12}r_{14}r_{23} + r_{34}r_{14}r_{23} + r_{12}r_{34}r_{23}) + c^4 r_{12}r_{34}r_{14}r_{23} \big] \times \Big(1 + A(x_1+x_2+r_1x_1+r_2x_2 - x_3 - x_4 - r_3x_3 - r_4x_4 + x_1 + x_4 + r_1x_1 + r_4x_4 - x_2 - x_3 - r_2x_2 - r_3x_3) \Big) + A^2 \Big\{ -(x_1+x_2+r_1x_1+r_2x_2)(x_3+x_4+r_3x_3+r_4x_4)$$

$$+ (x_1+x_2+r_1x_1+r_2x_2)(x_1+x_4+r_1x_1+r_4x_4)$$

$$- (x_1+x_2+r_1x_1+r_2x_2)(x_2+x_3+r_2x_2+r_3x_3)$$

$$- (x_3+x_4+r_3x_3+r_4x_4)(x_1+x_4+r_1x_1+r_4x_4)$$

$$+ (x_3+x_4+r_3x_3+r_4x_4)(x_2+x_3+r_2x_2+r_4x_4)$$

$$- (x_1+x_4+r_1x_1+r_4x_4)(x_2+x_3+r_2x_2+r_3x_2) \Big\}$$

$$+ A^3 \Big\{ -(x_1+x_2+\tau_1 x_1+\tau_2 x_2)(x_3+x_4+\tau_3 x_3+\tau_4 x_4)(x_1+x_4+\tau_1 x_1+\tau_4 x_4)$$

$$+(x_1+x_2+\tau_1 x_1+\tau_2 x_2)(x_3+x_4+\tau_3 x_3+\tau_4 x_4)(x_2+x_3+\tau_2 x_2+\tau_3 x_3)$$

$$+(x_3+x_4+\tau_3 x_3+\tau_4 x_4)(x_1+x_4+\tau_1 x_1+\tau_4 x_4)(x_2+x_3+\tau_2 x_2+\tau_3 x_3)$$

$$-(x_1+x_2+\tau_1 x_1+\tau_2 x_2)(x_1+x_4+\tau_1 x_1+\tau_4 x_4)(x_2+x_3+\tau_2 x_2+\tau_3 x_3)\Big\}$$

$$+ A^4 \Big\{(x_1+x_2+\tau_1 x_1+\tau_2 x_2)(x_3+x_4+\tau_3 x_3+\tau_4 x_4)(x_1+x_4+\tau_1 x_1+\tau_4 x_4)(x_2+x_3+\tau_2 x_2+\tau_3 x_3)\Big\}\Big]\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4$$

We now write down the non-zero integrals occurring in I_2 and get

$$I_2 = \iiiint e^{-2n(\tau_1+\tau_2+\tau_3+\tau_4)} \Big[1 + c(\tau_{12}+\tau_{34}+\tau_{14}+\tau_{23}) + c^2(\tau_{12}\tau_{34}+\tau_{12}\tau_{14}+\tau_{12}\tau_{23}$$

$$+\tau_{34}\tau_{14}+\tau_{34}\tau_{23}+\tau_{14}\tau_{23}) + c^3(\tau_{12}\tau_{34}\tau_{14}+\tau_{12}\tau_{34}\tau_{23}$$

$$+\tau_{34}\tau_{14}\tau_{23}+\tau_{12}\tau_{14}\tau_{23}) + c^4\tau_{12}\tau_{34}\tau_{14}\tau_{23}\Big]\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4$$

$$+ A^2 \iiiint \Big[\Big\{(x_1^2+2\tau_1 x_1^2+\tau_1^2 x_1^2) - (x_2^2+2\tau_2 x_2^2+\tau_2^2 x_2^2) - (x_4^2+2\tau_4 x_4^2+\tau_4^2 x_4^2)$$

$$+(x_3^2+2\tau_3 x_3^2+\tau_3^2 x_3^2)\Big\} e^{-2n(\tau_1+\tau_2+\tau_3+\tau_4)} \Big\{1 + c(\tau_{12}+\tau_{34}+\tau_{14}+\tau_{23})$$

$$+c^2(\tau_{12}\tau_{34}+\tau_{12}\tau_{14}+\tau_{12}\tau_{23}+\tau_{34}\tau_{14}+\tau_{34}\tau_{23}+\tau_{14}\tau_{23})$$

$$+c^3(\tau_{12}\tau_{34}\tau_{14}+\tau_{12}\tau_{34}\tau_{23}+\tau_{12}\tau_{14}\tau_{23}+\tau_{34}\tau_{14}\tau_{23})$$

$$+c^4\tau_{12}\tau_{34}\tau_{14}\tau_{23}\Big\}\Big]\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4$$

$$+ A^4 \iiiint \Big\{1+(\tau_1+\tau_3)+\tau_1\tau_3\Big\}^2 x_1^2 x_3^2\, e^{-2n(\tau_1+\tau_2+\tau_3+\tau_4)} \Big[1 + c(\tau_{12}+\tau_{34}+\tau_{14}+\tau_{23}) + c^2(\tau_{12}\tau_{34}$$

$$+\tau_{12}\tau_{14}+\tau_{12}\tau_{23}+\tau_{34}\tau_{14}+\tau_{34}\tau_{23}+\tau_{14}\tau_{23}) + c^3(\tau_{12}\tau_{34}\tau_{14}+\tau_{12}\tau_{34}\tau_{23}$$

$$+\tau_{12}\tau_{14}\tau_{23}+\tau_{34}\tau_{23}\tau_{14}) + c^4\tau_{12}\tau_{34}\tau_{14}\tau_{23}\Big]\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4$$

In the above expression for I_2 we notice tht the term whose coefficient is A^2 does not contribute anything because of the four parts which it has two are positive and the other two negative and each of them has the same numerical value. Thus I_2 reduces to simple form

$$
\begin{aligned}
I_2 = \iiiint & e^{-2n(\gamma_1+\gamma_2+\gamma_3+\gamma_4)} \Big[1 + c(\gamma_{12} + \gamma_{34} + \gamma_{14} + \gamma_{23}) + c^2(\gamma_{12}\gamma_{34} + \gamma_{12}\gamma_{34} + \gamma_{12}\gamma_{23} \\
& + \gamma_{34}\gamma_{14} + \gamma_{34}\gamma_{23} + \gamma_{14}\gamma_{23}) + c^3(\gamma_{12}\gamma_{34}\gamma_{14} + \gamma_{12}\gamma_{34}\gamma_{23} + \gamma_{12}\gamma_{14}\gamma_{23} \\
& + \gamma_{34}\gamma_{14}\gamma_{23}) + c^4\gamma_{12}\gamma_{34}\gamma_{14}\gamma_{23} \Big] \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4
\end{aligned}
$$

$$
\begin{aligned}
+ A^4 \iiiint & \Big[1 + (\gamma_1+\gamma_3) + \gamma_1\gamma_3 \Big]^2 x_1^2 x_3^2 \, e^{-2n(\gamma_1+\gamma_2+\gamma_3+\gamma_4)} \Big[1 + c(\gamma_{12} + \gamma_{34} + \gamma_{14} + \gamma_{23}) \\
& + c^2(\gamma_{12}\gamma_{34} + \gamma_{12}\gamma_{14} + \gamma_{12}\gamma_{23} + \gamma_{34}\gamma_{14} + \gamma_{34}\gamma_{23} + \gamma_{14}\gamma_{23}) \\
& + c^2(\gamma_{12}\gamma_{34}\gamma_{14} + \gamma_{12}\gamma_{34}\gamma_{23} + \gamma_{12}\gamma_{14}\gamma_{23} + \gamma_{34}\gamma_{14}\gamma_{23}) \\
& + c^4\gamma_{12}\gamma_{34}\gamma_{14}\gamma_{23} \Big] \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4
\end{aligned}
$$

and since we know that A^4 will be very small and so we neglect this term, finally having

$$
\begin{aligned}
I_2 = & \iiiint e^{-2n(\gamma_1+\gamma_2+\gamma_3+\gamma_4)} \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4 \\
& + 4c \iiiint \gamma_{12} \, e^{-2n(\gamma_1+\gamma_2+\gamma_3+\gamma_4)} \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4 \\
& + 2c^2 \iiiint \gamma_{12}\gamma_{34} \, e^{-2n(\gamma_1+\gamma_2+\gamma_3+\gamma_4)} \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4 \\
& + 4c^2 \iiiint \gamma_{12}\gamma_{14} \, e^{-2n(\gamma_1+\gamma_2+\gamma_3+\gamma_4)} \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4
\end{aligned}
$$

$$+ 4c^3 \iiiint r_{12} r_{34} r_{14} \, e^{-2n(r_1+r_2+r_3+r_4)} \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4$$

$$+ c^4 \iiiint r_{12} r_{34} r_{14} r_{23} \, e^{-2n(r_1+r_2+r_3+r_4)} \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4$$

because the integrals grouped together have each the same value. The values of these integrals are listed in the following table. The last one in C^4 is again neglected due to its being very small and tedious to evaluate.

No.		Values
1.	$\frac{\pi^4}{n^{12}}$	$= .0609$
2.	$4c\left[\frac{\pi^2}{n^6} \times \frac{35\pi^2}{16n^7}\right] = \frac{35\pi^4 c}{4n^{13}} =$	$.1051$
3.	$2c^2\left(\frac{35\pi^2}{6n^7}\right)^2 + 4c^2 \frac{\pi^4}{n^{14}} \times \frac{1501}{288}$	$= .0226 + .0492$
4.	$4c^3 \times \frac{\pi^4}{n^{15}} \times 11.8895$	$= .0220$

So the integral $I_2 = .2372$

Now we proceed to calculate H_2.

$$H_2 = R^3 \int V \psi_1(1,2) \, \psi_2(3,4) \, \psi_1(1,4) \, \psi_2(2,3) \, d\tau$$

$$= \iiiint \Big[(x_1x_3 + y_1y_3 - 2z_1z_3) + (x_1x_4 + y_1y_4 - 2z_1z_4) + (x_2x_3 + y_2y_3 - 2z_2z_3) + (x_2x_4 + y_2y_4 - 2z_2z_4) \Big] \psi_1(1,2) \, \psi_2(3,4) \, \psi_1(1,4) \, \psi_2(2,3) \, d\tau_1 d\tau_2 d\tau_3 d\tau_4$$

$$= \iiiint (x_1x_3 + x_2x_3 + x_1x_4 + x_2x_4)\, \psi_1(1,2)\, \psi_2(3,4)\, \psi_1(1,4)\, \psi_2(2,3)\, d\tau_1 d\tau_2 d\tau_3 d\tau_4$$

because $\psi_1(1,2)\ \psi_2(3,4)\ \psi_1(1,4)\ \psi_2(2,3)$ does not contain y's and z's and so integration over these will give zero.

$$\begin{aligned}
\text{So}\quad H_2 = \iiiint \Big\{ &(x_1x_3 + x_1x_4 + x_2x_3 + x_2x_4)\, e^{-2n(r_1+r_2+r_3+r_4)} \big[1 + c\,(r_{12} + r_{34} + r_{14} + r_{23}) \\
&+ c^2 (r_{12}r_{34} + r_{12}r_{14} + r_{12}r_{23} + r_{34}r_{14} + r_{34}r_{23} + r_{14}r_{23}) \\
&+ c^3 (r_{12}r_{34}r_{14} + r_{12}r_{34}r_{23} + r_{12}r_{14}r_{23} + r_{34}r_{14}r_{23}) + c^4 r_{12}r_{34}r_{14}r_{23} \big] \times \\
&\big[1 + A\,(2x_1 + 2x_1r_1 - 2x_3 - 2x_3r_3) + A^2 \big\{ -(x_1x_3 + x_1x_4 + \\
&r_3x_1x_3 + r_1x_1x_4 + x_2x_3 + x_2x_4 + r_3x_2x_3 + r_4x_2x_4 + r_1x_1x_3 \\
&+ r_1x_1x_4 + r_1r_3x_1x_3 + r_1r_4x_1x_4 + r_2x_2x_3 + r_2x_2x_4 + r_2r_3x_2x_3 \\
&+ r_2r_4x_2x_4) + (x_1^2 + x_1x_4 + r_1x_1^2 + r_4x_1x_4 + x_1x_2 + x_2x_4 \\
&+ r_1x_1x_2 + r_4x_2x_4 + r_1x_1^2 + r_1x_1x_4 + r_1^2x_1^2 + r_1r_4x_1x_4 + r_2x_1x_2 \\
&+ r_2x_2x_4 + r_1r_2x_1x_2 + r_2r_4x_2x_4) - (x_1x_2 + x_1x_3 + r_2x_1x_2 \\
&+ r_3x_1x_3 + x_2^2 + x_2x_3 + r_2x_2^2 + r_3x_2x_3 + r_1x_1x_2 + r_1x_1x_3 \\
&+ r_1r_2x_1x_3 + r_1r_3x_1x_3 + r_2x_2^2 + r_2x_2x_3 + r_2^2x_2^2 + r_2r_3x_2x_3) \\
&- (x_3x_1 + x_3x_4 + r_1x_1x_3 + r_4x_3x_4 + x_1x_4 + x_4^2 + r_1x_1x_4 \\
&+ r_2x_2x_4 + r_3x_1x_3 + r_3x_3x_4 + r_1r_3x_1x_3 + r_4r_3x_3x_4 \\
&+ r_4x_1x_4 + r_1^2x_4^2 + r_1r_4x_1x_4 + r_4^2x_4^2) + (x_2x_3 + x_3^2 \\
&+ r_2x_2x_3 + r_3x_3^2 + x_2x_4 + x_3x_4 + r_2x_2x_4 + r_3x_3x_4 \\
&+ r_3x_2x_3 + r_3x_3^2 + r_2r_3x_2x_3 + r_3^2x_3^2 + r_4x_2x_4 +
\end{aligned}$$

$$+ \gamma_4 x_3 x_4 + \gamma_2 \gamma_4 x_2 x_4 + \gamma_3 \gamma_4 x_3 x_4) - (x_1 x_2 + x_1 x_3 + \gamma_2 x_1 x_2$$

$$+ \gamma_3 x_1 x_3 + x_2 x_4 + x_3 x_4 + \gamma_2 x_2 x_4 + \gamma_3 x_3 x_4 + \gamma_1 x_1 x_2 + \gamma_1 x_1 x_3$$

$$+ \gamma_1 \gamma_2 x_1 x_2 + \gamma_1 \gamma_3 x_1 x_3 + \gamma_4 x_2 x_4 + \gamma_4 x_3 x_4 + \gamma_2 \gamma_4 x_2 x_4 + \gamma_3 \gamma_4 x_3 x_4)\}$$

$$+ A^3 \text{ and } A^4 \text{ terms}]\} d\gamma_1 \, d\gamma_2 \, d\gamma_3 \, d\gamma_4$$

$$= \iiiint \Big\{ (x_1 x_3 + x_1 x_4 + x_2 x_3 + x_2 x_4) e^{-2n(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4)} \Big[1 + c(\gamma_{12} + \gamma_{34} + \gamma_{14} + \gamma_{23}) + c^2(\gamma_{12}\gamma_{34}$$

$$+ \gamma_{12}\gamma_{14} + \gamma_{12}\gamma_{23} + \gamma_{34}\gamma_{14} + \gamma_{34}\gamma_{23} + \gamma_{14}\gamma_{23}) + c^3(\gamma_{12}\gamma_{34}\gamma_{14} + \gamma_{12}\gamma_{34}\gamma_{23}$$

$$+ \gamma_{12}\gamma_{14}\gamma_{23} + \gamma_{34}\gamma_{14}\gamma_{23}) + c^4 \gamma_{12}\gamma_{34}\gamma_{14}\gamma_{23} \Big] \times \Big[A^2 \{ -4(1 + \gamma_1 + \gamma_3$$

$$+ \gamma_1 \gamma_3) x_1 x_3 - (1 + \gamma_4 + \gamma_1 + \gamma_1 \gamma_4) x_1 x_4 - (1 + \gamma_2 + \gamma_3 + \gamma_2 \gamma_3) x_2 x_3 \}$$

$$+ A^2 \{ \; ---- \; \} \Big] \Big\} d\gamma_1 \, d\gamma_2 \, d\gamma_3 \, d\gamma_4$$

In the above we have excluded terms having A and A^3 as they become zero. In addition to those the parts of A^2 and A^4 terms will integrate to zero. If we again leave out A^4 term as very small we get

$$H_2 = -4A^2 \iiiint x_1^2 x_3^2 (1 + \gamma_1 + \gamma_3 + \gamma_1 \gamma_3) e^{-2n(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4)} \cdot \Big[1 + c(\gamma_{12} + \gamma_{34} + \gamma_{14} + \gamma_{23})$$

$$+ c^3(\gamma_{12}\gamma_{34}\gamma_{14} + \gamma_{12}\gamma_{34}\gamma_{23} + \gamma_{12}\gamma_{14}\gamma_{23} + \gamma_{34}\gamma_{14}\gamma_{23})$$

$$+ c^2(\gamma_{12}\gamma_{34} + \gamma_{12}\gamma_{14} + \gamma_{12}\gamma_{23} + \gamma_{34}\gamma_{14} + \gamma_{34}\gamma_{23} + \gamma_{14}\gamma_{23})$$

$$+ c^4 \gamma_{12}\gamma_{34}\gamma_{14}\gamma_{23} \Big] d\gamma_1 \, d\gamma_2 \, d\gamma_3 \, d\gamma_4$$

$$- A^2 \iiiint x_1^2 x_4^2 \left(1 + r_1 + r_4 + r_1 r_4\right) e^{-2n(r_1+r_2+r_3+r_4)} \left[1 + c\left(r_{12} + r_{34} + r_{14} + r_{23}\right) \right.$$

$$+ c^2 \left(r_{12} r_{34} + r_{12} r_{14} + r_{12} r_{23} + r_{34} r_{14} + r_{34} r_{23} + r_{14} r_{23}\right)$$

$$+ c^3 \left(r_{12} r_{34} r_{14} + r_{12} r_{34} r_{23} + r_{12} r_{14} r_{23} + r_{34} r_{14} r_{23}\right)$$

$$\left. + c^4 r_{12} r_{34} r_{14} r_{23} \right] d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4$$

$$- A^2 \iiiint x_2^2 x_3^2 \left(1 + r_2 + r_3 + r_2 r_3\right) e^{-2n(r_1+r_2+r_3+r_4)} \left[1 + c\left(r_{12} + r_{34} + r_{14} + r_{23}\right) \right.$$

$$+ c^2 \left(r_{12} r_{34} + r_{12} r_{14} + r_{12} r_{23} + r_{34} r_{14} + r_{34} r_{23} + r_{14} r_{23}\right)$$

$$+ c^3 \left(r_{12} r_{34} r_{14} + r_{12} r_{34} r_{23} + r_{34} r_{14} r_{23} + r_{12} r_{14} r_{23}\right)$$

$$\left. + c^4 r_{12} r_{34} r_{14} r_{23} \right] d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4$$

$$= - \frac{6A^2}{9} \iiiint r_1^2 r_3^2 \left(1 + r_1 + r_3 + r_1 r_3\right) e^{-2n(r_1+r_2+r_3+r_4)} \left[1 + c\left(r_{12} + r_{34} + r_{14} + r_{23}\right) \right.$$

$$+ c^2 \left(r_{12} r_{34} + r_{12} r_{14} + r_{12} r_{23} + r_{34} r_{14} + r_{34} r_{23} + r_{14} r_{23}\right)$$

$$\left. + c^3 \left(r_{12} r_{34} r_{14} + r_{12} r_{34} r_{23} + r_{12} r_{14} r_{23} + r_{34} r_{14} r_{23}\right) \right] d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4$$

where we have replaced x_1^2 and x_3^2 by $\frac{1}{3} r_1^2$ and $\frac{1}{3} r_3^2$ respectively and all integrals in H_2 have the same value on account of symmetry. Thus

$$H_2 = - \frac{2A^2}{3} \iiiint r_1^2 r_3^2 \left(1 + r_1 + r_3 + r_1 r_3\right) e^{-2n(r_1+r_2+r_3+r_4)} \left[1 + c\left(r_{12} + r_{34} + r_{14} + r_{23}\right) \right.$$

$$+ c^2 \left(r_{12} r_{34} + r_{12} r_{14} + r_{12} r_{23} + r_{34} r_{14} + r_{34} r_{23} + r_{14} r_{23}\right)$$

$$+ c^3 \left(r_{12} r_{34} r_{14} + r_{12} r_{34} r_{23} + r_{12} r_{14} r_{23} + r_{34} r_{14} r_{23}\right)$$

$$\left. + c^4 r_{12} r_{34} r_{14} r_{23} \right] d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4$$

and we have the following integrals whose evaluated values are listed along with the integrals.

$$(1)\quad \iiiint r_1^2 r_3^2\, e^{-2n(r_1+r_2+r_3\ r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{9\pi^4}{n^{16}} = .0464$$

$$(2)\quad \iiiint r_1^3 r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{45\pi^4}{2n^{17}} = .0628$$

$$(3)\quad \iiiint r_1^2 r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{45\pi^4}{2n^{17}} = .0628$$

$$(4)\quad \iiiint r_1^3 r^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{225\pi^4}{4n^{18}} = .0849$$

$$(5)\quad c\iiiint r_{12}\, r_1^2 r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c}{n^{17}} \times \frac{1701}{64} = .0270$$

$$(6)\quad c\iiiint r_{12}\, r_1^3 r_3^2\, e^{-2n(r_1+r_2+r_3+r_4}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 \quad \frac{3\pi^4 c}{} \times \frac{6489}{256} = .0418$$

$$(7)\quad c\iiiint r_{12}\, r_1^2 r_3^3\, e^{-2n(r_1+r_2+r_3+r_4}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{15\pi^4 c}{n^{18}} \times \frac{567}{128} = .0365$$

$$(8)\quad c\iiiint r_{12}\, r_1^3 r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{15\pi^4 c}{n^{19}} \times \frac{6489}{512} = .0565$$

$$(9)\quad c\iiiint r_{34}\, r_1^2 r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c}{n^{17}} \times \frac{1701}{64} = .0270$$

$$(10)\quad c\iiiint r_{34}\, r_1^3 r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{3\pi^4 c}{n^{18}} \times \frac{6489}{256} = .0418$$

$$(11)\quad c\iiiint r_{34}\, r_1^2 r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{15\pi^4 c}{n^{18}} \times \frac{567}{128} = .0365$$

(12) $$c\iiiint r_{34}\, r_1^{3} r_3^{3}\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{15\pi^4 c}{n^{19}}\times\frac{6489}{512} = .0565$$

(13) $$c\iiiint r_{14}\, r_1^{2} r_3^{2}\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c}{n^{17}}\times\frac{1701}{64} = .0270$$

(14) $$c\iiiint r_{14}\, r_1^{3} r_3^{2}\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{3\pi^4 c}{n^{18}}\times\frac{6489}{256} = .0418$$

(15) $$c\iiiint r_{14}\, r_1^{2} r_3^{3}\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{15\pi^4 c}{n^{18}}\times\frac{567}{128} = .0365$$

(16) $$c\iiiint r_{14}\, r_1^{3} r_3^{3}\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{15\pi^4 c}{n^{19}}\times\frac{6489}{512} = .0565$$

(17) $$c\iiiint r_{23}\, r_1^{2} r_3^{2}\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c}{n^{17}}\times\frac{1701}{64} = .0270$$

(18) $$c\iiiint r_{23}\, r_1^{3} r_3^{2}\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{15\pi^4 c}{n^{18}}\times\frac{567}{128} = .0365$$

(19) $$c\iiiint r_{23}\, r_1^{2} r_3^{3}\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{3\pi^4 c}{n^{18}}\times\frac{6489}{256} = .0418$$

(20) $$c\iiiint r_{23}\, r_1^{3} r_3^{3}\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{15\pi^4 c}{n^{19}}\times\frac{6489}{512} = .0565$$

(21) $$c^2\iiiint r_{12}\, r_{34}\, r_1^{2} r_3^{2}\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{18}}\times\left(\frac{567}{64}\right)^2 = .0157$$

(22) $$c^2\iiiint r_{12}\, r_{34}\, r_1^{3} r_3^{2}\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{19}}\times\frac{6489\times 567}{2^{14}} = .0243$$

(23) $$c^2\iiiint r_{12}\, r_{34}\, r_1^{2} r_3^{3}\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{19}}\times\frac{6489\times 567}{2^{14}} = .0243$$

(24) $$c^2 \iiiint r_{12}\, r_{34}\, r_1^3 r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{20}} \times \frac{(6489)^2}{2^{16}} = .0376$$

(25) $$c^2 \iiiint r_{12}\, r_{14}\, r_1^2 r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{3\pi^4 c^2}{n^{18}} \times \frac{921.38}{2^5} = .0172$$

(26) $$c^2 \iiiint r_{12}\, r_{14}\, r_1^3 r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{3\pi^4 c^2}{n^{19}} \times \frac{1961460.3}{2^6 \times 324} = .0307$$

(27) $$c^2 \iiiint r_{12}\, r_{14}\, r_1^2 r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{15\pi^4 c^2}{n^{19}} \times \frac{921.38}{2^6} = .0234$$

(28) $$c^2 \iiiint r_{12}\, r_{14}\, r_1^3 r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{15\pi^4 c^2}{n^{20}} \times \frac{1961460.3}{2^7 \times 324} = .0415$$

(29) $$c^2 \iiiint r_{12}\, r_{23}\, r_1^2 r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{18}} \times \frac{5279.8}{2^7} = .0082$$

(30) $$c^2 \iiiint r_{12}\, r_{23}\, r_1^3 r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{19}} \times \frac{42483.12}{2^8} = .0179$$

(31) $$c^2 \iiiint r_{12}\, r_{23}\, r_1^2 r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{19}} \times \frac{42483.12}{2^8} = .0179$$

(32) $$c^2 \iiiint r_{12}\, r_{23}\, r_1^3 r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{20}} \times \frac{123174.51}{2^9} = .0141$$

(33) $$c^2 \iiiint r_{34}\, r_{14}\, r_1^2 r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{18}} \times \frac{5279.8}{2^7} = .0082$$

(34) $$c^2 \iiiint r_{34}\, r_{14}\, r_1^3 r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{19}} \times \frac{42483.12}{2^8} = .0179$$

(35) $$c^2 \iiiint r_{34}\, r_{14}\, r_1^2 r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{19}} \times \frac{42483.12}{2^8} = .0179$$

(36) $$c^2 \iiiint r_{34}\, r_{14}\, r_1^3\, r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{20}} \times \frac{123174.51}{2^8} = .0141$$

(37) $$c^2 \iiiint r_{34}\, r_{23}\, r_1^2\, r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{3\pi^4 c^2}{n^{18}} \times \frac{921.38}{2^5} = .0173$$

(38) $$c^2 \iiiint r_{34}\, r_{23}\, r_1^3\, r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{3\pi^4 c^2}{n^{19}} \times \frac{1961460.3}{324} = .0307$$

(39) $$c^2 \iiiint r_{34}\, r_{23}\, r_1^2\, r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{15\pi^4 c^2}{n^{19}} \times \frac{921.38}{2^6} = .0234$$

(40) $$c^2 \iiiint r_{34}\, r_{23}\, r_1^3\, r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{15\pi^4 c^2}{n^{20}} \times \frac{1961460.3}{2^7 \times 324} = .041$$

(41) $$c^2 \iiiint r_{14}\, r_{23}\, r_1^2\, r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{15}} \times \left(\frac{567}{64}\right)^2 = .0157$$

(42) $$c^2 \iiiint r_{14}\, r_{23}\, r_1^3\, r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{19}} \times \frac{6489 \times 567}{2^{14}} = .0243$$

(43) $$c^2 \iiiint r_{14}\, r_{23}\, r_1^2\, r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{19}} \times \frac{6489 \times 567}{2^{14}} = .0243$$

(44) $$c^2 \iiiint r_{14}\, r_{23}\, r_1^3\, r_3^3\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^2}{n^{20}} \times \frac{(6489)^2}{2^{16}} = .0376$$

(45) $$c^3 \iiiint r_{12}\, r_{34}\, r_{14}\, r_1^2\, r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^3}{n^{19}} \times 301.15 = .0118$$

(46) $$c^3 \iiiint r_{12}\, r_{34}\, r_{14}\, r_1^3\, r_3^2\, e^{-2n(r_1+r_2+r_3+r_4)}\, d\tau_1\, d\tau_2\, d\tau_3\, d\tau_4 = \frac{\pi^4 c^3}{n^{20}} \times 871.37 = .0185$$

(47) $c^3 \iiiint r_{12} r_{34} r_{14} r_1^2 r_3^3 e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{20}} \times 576.84 = .0123$

(48) $c^3 \iiiint r_{12} r_{34} r_{14} r_1^3 r_3^3 e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{21}} \times 2231.52 = .0256$

(49) $c^3 \iiiint r_{12} r_{34} r_{23} r_1^2 r_3^2 e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{19}} \times 301.15 = .0118$

(50) $c^3 \iiiint r_{12} r_{34} r_{23} r_1^3 r_3^2 e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{20}} \times 871.37 = .0185$

(51) $c^3 \iiiint r_{12} r_{34} r_{23} r_1^2 r_3^3 e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{20}} \times 576.84 = .0123$

(52) $c^3 \iiiint r_{12} r_{34} r_{23} r_1^3 r_3^3 e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{21}} \times 2231.52 = .0256$

(53) $c^3 \iiiint r_{34} r_{14} r_{23} r_1^2 r_3^2 e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{19}} \times 301.15 = .0118$

(54) $c^3 \iiiint r_{34} r_{14} r_{23} r_1^3 r_3^2 e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{20}} \times 871.37 = .0185$

(55) $c^3 \iiiint r_{34} r_{14} r_{23} r_3^3 r_1^2 e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{20}} \times 576.84 = .0123$

(56) $c^3 \iiiint r_{34} r_{14} r_{23} r_1^3 r_3^3 e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{21}} \times 2231.52 = .0256$

(57) $c^3 \iiiint r_{12} r_{14} r_{23} r_1^2 r_3^2 e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{19}} \times 301.15 = .0118$

(58) $c^3 \iiiint r_{12} r_{14} r_{23} r_1^3 r_3^2 e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{20}} \times 871.37 = .0185$

$$(59) \quad c^3 \iiiint r_{12} r_{14} r_{23} r_1^{-2} r_3^{-3} e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{20}} \times 576.84 = .0123$$

$$(60) \quad c^3 \iiiint r_{12} r_{14} r_{23} r_1^{-3} r_3^{-3} e^{-2n(r_1+r_2+r_3+r_4)} d\tau_1 d\tau_2 d\tau_3 d\tau_4 = \frac{\pi^4 c^3}{n^{21}} \times 2231.52 = .0257$$

The value of H_2 neglecting C^4 terms is obtained from these

$$H_2 = -\frac{2}{3} A^2 \times 1.7226$$

$$= -.1197 \times 2F^2$$

This leads to a value of ΔE_1 given by

$$\Delta E_1 = -\frac{F^2}{R^3} \times \frac{.4128 - .3394}{(.2671 + .3606 F^2 + .1216 F^4) - 2 \times .2372}$$

$$= -\frac{F^2}{R^3} \times \frac{.0734}{.2023}$$

$$= -\frac{F^2}{R^3} \times .3628$$

$$= -\frac{.00009}{R^3} \quad \text{Hartree units}$$

$$= -\frac{.0039 \times 10^{-12}}{R^3} \quad \text{ergs}$$

REFERENCES

(1) Keesom, W. H., and Schmidt, G., 1933, Comm. Leiden, 226b

(2) Keesom, W. H., and Schweers, J., 1941, Physica, 8, 1020, 1032

(3) Langmuir, I., 1918, Jour. Amer. Chem. Soc., 40, 1361

(4) Frederiske, H. P. R., and Gorter, C. J., 1950, Physica, 16, 403

(5) Schaeffer, W. D., Smith, W. R., and Wendell, C. B., 1949, Jour. Chem. Soc., 71, 863

(6) Long, E., and Meyer, L., 1951, Phy. Rev., 84, 551; 1952, ibid, 85, 1035

(7) Mastrangelo, S. V. R., and Aston, J. G., 1951, Jour. Chem. Phy., 19, 1370

(8) Strauss, A. J., 1952, Thesis, Chicago

(9) Brunauer, St., Emmet, P. H., and Teller, E., 1938, Jour. Amer. Chem. Soc., 60, 309

(10) Band, W., 1949, Phys. Rev., 76, 441; 1951, J. Chem. Phy., 19, 435

(11) Margenau, H., 1931, Phys. Rev., 38, 747

(12) Slater, J. C. and Kirkwood, J. G., 1931, Phys. Rev., 37, 682

(13) Margenau, H., loc. cit.

(14) Hasse', H. R., 1930, Proc. Cambr. Phil. Soc., 26, 542

(15) Dushman, S., Elements of Quantum Mechanics (1938), John Wiley & Sons p. 265

(16) Slater, J. C., (1928), Phys. Rev., 32, 355